THE PREDICTION OF HYDROCARBON TRANSPORT VIA COPEPOD FECAL PELLETS

A

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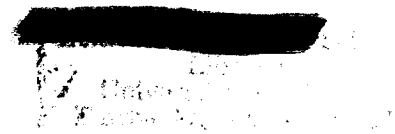

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VIA COPEPOD FECAL PELLETS

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ABSTRACT

Copepod feces are an important mechanism in transport of nutrients to depths. In this thesis, I examine potential for hydrocarbon transport via this mechanism and the consequent potential for benthic disturbance.

Examination of present knowledge of copepod feeding behavior resulted in development of a model for estimating hydrocarbon transfer into feces. Maximum transfer is predicted at 200 mg $m^{-3}day^{-1}$ in the Bering Sea; 60 mg m^{-3} day^{-1} in Port Valdez. Spring bloom and summer months with high numbers of zooplankton and phytoplankton present the optimum time for transfer. Winter conditions are most stressful for the animals. Ambient phytoplankton characteristics and the animals' desired daily rations are postulated to determine the amount of oil transferred. Toxic effects resulting from transfer of oil droplets are likely to result from the energetic costs of transferring the oil and the accumulation of refractory compounds.

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CHAPTER 1

INTRODUCTION

The objective of this thesis project has been to develop an understanding of the potential transfer of hydrocarbons via zooplankton fecal pellets from the surface layers of the ocean to sediments, and to other organisms. The basis of this study is information in the literature on: a) oil spill observations, b) oiling experiments detailing toxicity and hydrocarbon transfer, c) copepod feeding behavior, d) baseline hydrocarbons in the food web and dissolved in the water column, and e) biogenic hydrocarbon transfer within the food web. The major geographic area of interest for this study is the Alaskan coastline, including both arctic and sub-arctic waters. Therefore, baseline hydrocarbon analyses were made on plankton samples from the Bering Sea and from Cook Inlet to give an experimental base for the area on which the study is made.

Fecal pellets are the object of interest for this study because they serve as an important natural nutrient transfer mechanism, providing rapid transit of nutrients from the pelagic system to the benthos and to other organisms which ingest them (Schrader, 1971). The importance of this notion in terms of the consequences of exposure to oil pollution is that ecologically the pelagic system, especially the plankton, is more resilient to perturbations and stress than the benthos or higher trophic levels. Plankton populations naturally bloom and crash, experience large fluctuations in nutrient supply and ambient conditions, and are subject to successional patterns over short-term periods. The benthos and higher trophic levels, however, function in more of a steady-state environment.

Fecal pellets may provide the critical and disastrous link in exposing these ecological areas to a stress that would otherwise filter through over a much longer time period.

There are many gaps in present-day knowledge concerning the processes which would interact to produce an oil-laden fecal pellet. As a tool in understanding the role of fecal transport in arctic and subarctic systems, this study resulted in the development of a numerical model describing copepod fecal transport of hydrocarbons. The quantitative predictions are obviously subject to many errors and so must be considered order-of-magnitude calculations. As such, they have value in delineating directions of flux and gross areas of impact. Furthermore, they provide a first estimation of the potential seriousness of impact. The utility of this tool is in clarification of critical processes in fecal transport, the degree to which a change in process rate will affect total transport, and key areas where more knowledge is vital.

CHAPTER 2

THE MODEL

Theory

The theoretical basis used for construction of this model describing transfer of oil into copepod fecal pellets is limited to the prediction of ingestion of metabolically inert oil particles by size-selective poikilothermic filter feeders. Production of fecal pellets depends on the quality and quantity of ingested material and the assimilation efficiency of the animal (Turner, 1977a). The restriction of metabolic inertness demands adjustment in assumptions concerning assimilation efficiency, since the additional material in the gut can be assumed to impede activity of the digestive enzymes. Poikilothermic animals have different feeding stimuli and energy storage strategies than the more intensively studied homeotherms so feeding models must reflect this difference. Appendix I includes a section on feeding models for poikilotherms.

Size-selectivity implies that ingestion of oil particles will be limited to those particles resembling the food particles normally fed upon. Oil droplet formation is not modeled. Oil droplet concentrations are stipulated in model calculations to resemble ambient phytoplankton levels in cell number and dimensions. The characteristics of the ambient phytoplankton determine grazer filtering rates and size selection (see Appendix I). The concentration of food particles relative to that of oil droplets is postulated to be important in determining grazing behavior and stress upon the animals, thus, seasonal effects will be

important. A lower boundary to the model is provided by a threshold feeding concentration below which animals will cease to filter. An upper limit is set at the oil droplet concentration above which the animals would expend more energy gathering inert particles than food (for a discussion of the processes of degradation of an oil spill and oil droplet formation, see Appendix II).

Observations both following oil spills and in the laboratory demonstrate that copepods will ingest oil and pass it into fecal pellets. After the *Argo Merchant* oil spill in 1977 copepods were collected from the area and treated with lactic acid to make them transparent. Oil was found on the external exoskeleton, on the feeding appendages, and within the intestine and gut (Maurer, 1977). In several studies, fecal pellets of copepods have been shown to contain oil. Experiments with *Calanus helgolandicus* exposed to oil concentrations of 10 ppm produced fecal pellets that sank quite slowly because they were half oil (Spooner and Corkett, 1974). Copepods observed after the *Torrey Canyon* oil spill were seen (via fluorescent tracer) to pass oil unchanged into fecal pellets (Parker *et al.*, 1970). Fecal pellets obtained from copepods after the wreck of the tanker *Arrow* contained up to 7% oil by mass which had no apparent effect on the animals (Conover, 1971). In Dabob Bay, Puget Sound, zooplankton fecal pellets have been shown to control the deposition of polycyclic aromatic hydrocarbons upon the sediments. The hydrocarbons proved to be chemically refractory although benthic respiration contributed to significant recycling of other fractions of the total organic carbon (Prahl and Carpenter, 1979).

Literature predictions of the amount of oil which may potentially be transferred into fecal pellets generally extrapolate from empirical observations of the content of oil in collected fecal pellets (Parker *et al.*, 1970; Conover, 1971). This model differs from these predictions in being primarily a theoretical examination of present understanding of copepod feeding behavior and the manner in which oil ingestion might occur and be controlled. Different input terms are also required. This model also postulates an upper limit for oil ingestion which may be used to estimate stress upon the population of grazers.

Model Terms

Table 1 is the worksheet for construction of this model. It lists the variables which may conceivably interact in the transfer process. The worksheet ends with a list of the variables incorporated into the model. They are: environmental conditions, maximum daily ration, population density, food present, and assimilation efficiency. Environmental conditions are not included as direct variables but influence the choice of values for the other terms. These are the input terms for which values must be set before model calculations. Tables are included in the appendices which list typical literature values for these variables, especially those available for Alaskan waters. Values in these tables are the basis of the model calculations in Chapter 3.

The sequence of transfer of hydrocarbons via copepod fecal pellets is considered to occur in the following four phases: 1) transformation of oil from the spill source into dispersed droplets in the water column, 2)

TABLE 1. Worksheet for model construction.

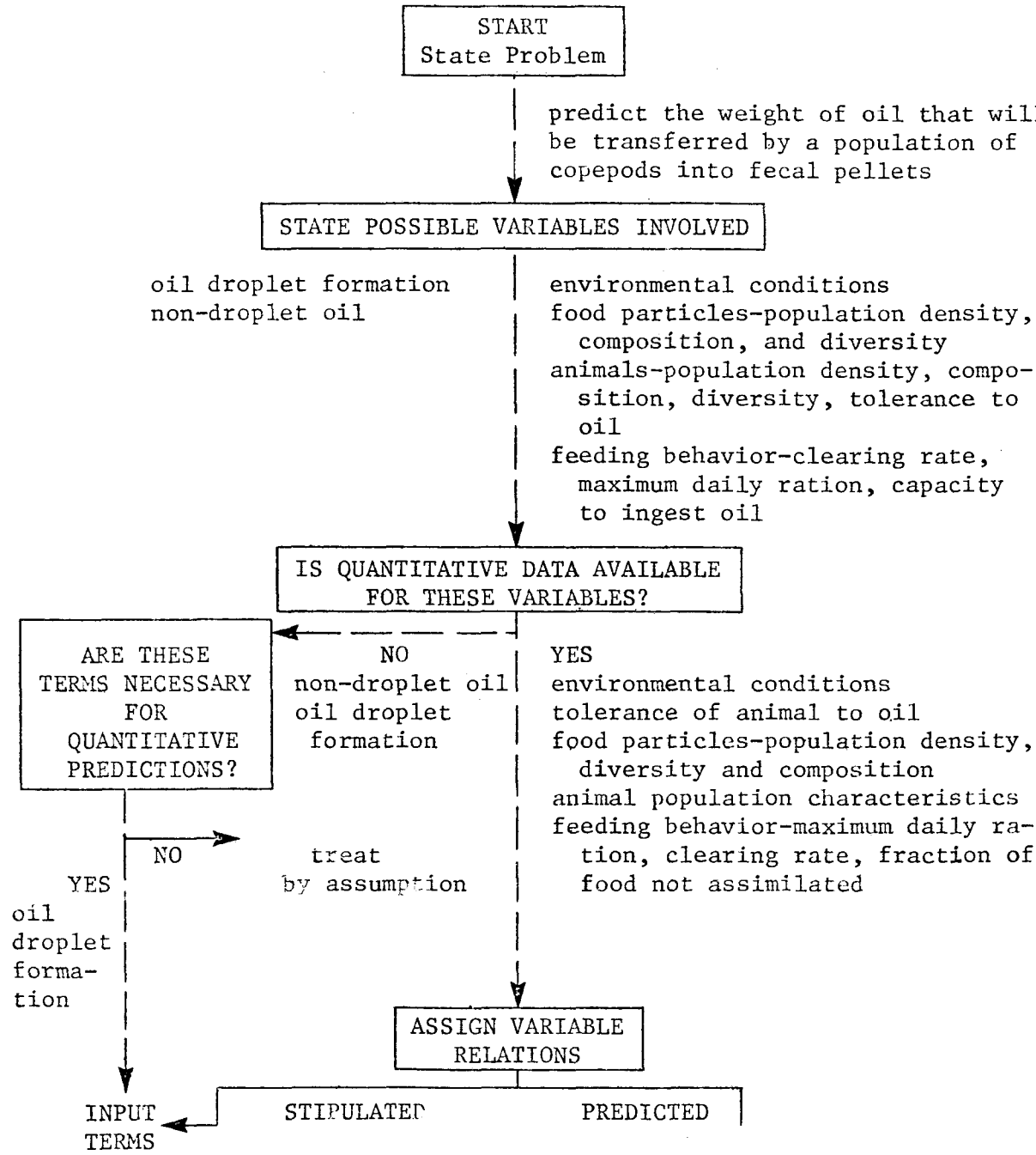
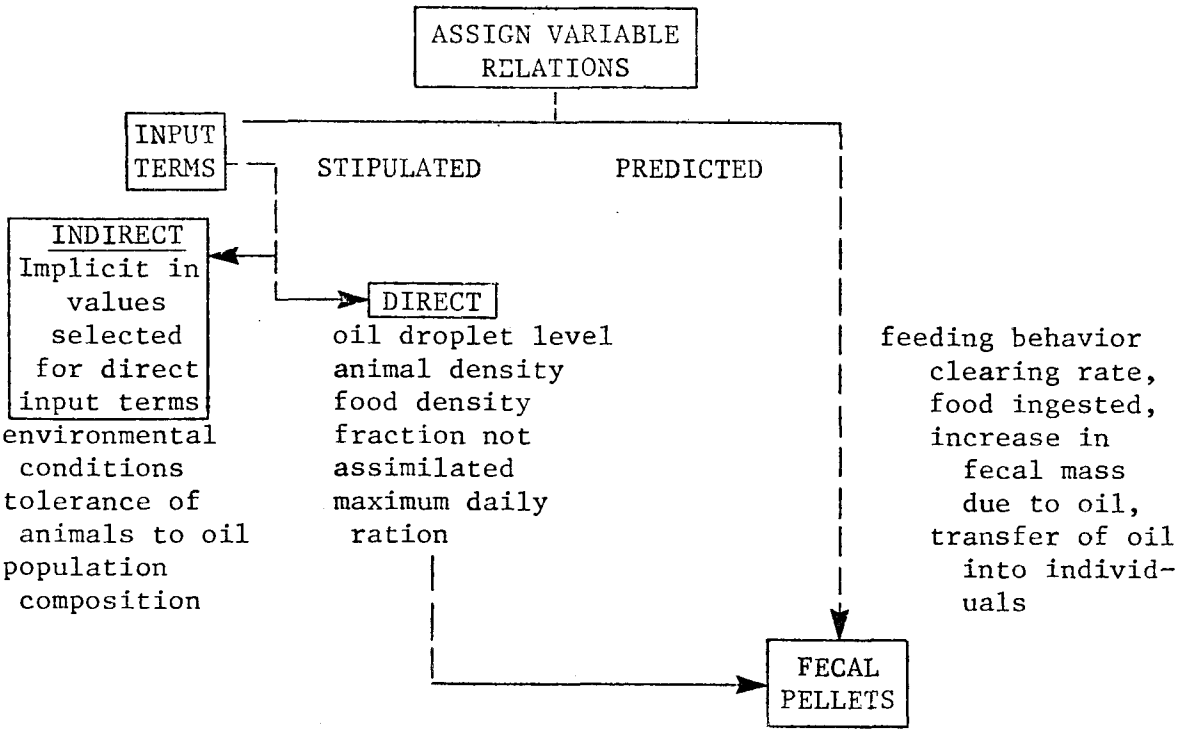


TABLE 1. Continued.



transport into individuals (ingestion), 3) transport into fecal pellets (egestion), and 4) transfer throughout the food web. This model makes quantitative predictions only for the second and third phases. Phases 1 (see Appendix II) and 4 (see Chapter 3 discussion) are discussed in some detail in order to indicate what factors will affect, and be affected by, the transport of oil into fecal pellets.

Model Assumptions

Table 2 summarizes the assumptions made for construction of the model. In the following pages the assumptions are stated more fully, and pertinent literature is cited when necessary. The assumptions listed in the lower portion of the table are those made for the incorporation of an upper limit into the model. These upper-limit assumptions are discussed in the sections preceding the explanation of the upper-limit equations.

Interaction of feeding behavior with oil droplets

In this model it is assumed that there will be no discrimination against oil droplets and that in the copepods normal searching and food grazing process (see Appendix I) as the oil particle is encountered, it will be ingested. Thus, the model is restricted to particles of oil within the size range a species is capable of ingesting, but ignores possible selection of particle size within that range. Treatment of the oil droplet as a normal food particle implies that the behavioral

TABLE 2. Assumptions.

Animals feed equally on each particle type (food and oil) according to their concentration in the water.
Presence of oil droplets or dissolved oil does not impair the animal or change its behavior (at the low oil levels used in model calculations).
Time necessary for generation of oil droplets is sufficient for toxic aromatic compounds to evaporate.
All oil ingested as oil droplets is excreted.
Fecal production rates are equal to those for copepods feeding on unoiled systems.
Uptake of soluble fractions from drinking water is negligible (see Appendix I).
The figures used for population density represent a population of uniform individuals.
The carbon biomass resulting from primary productivity is produced by uniform cells.
The inclusion of oil within fecal pellets will not lighten the pellet density to less than that of seawater.
Upper Limit Assumptions
Copepods will feed until they ingest daily rations necessary for maintenance.
Total ingested mass may not exceed twice the maximum daily ration.
An animal will cease to feed when the concentration of oil droplets exceeds the concentration of food particles.

rules and rates for food intake will apply for feeding in the presence of oil droplets.

This assumption is supported by observations of copepods following the spill of the tanker *Arrow* in Nova Scotia. Forrester (1971) reports a maximum oil concentration resulting from this spill of 0.02 g m^{-3} with many particles less than 1 mm present. Conover (1971) found that 0.7% of the food ingested by the copepods present at this time was oil. He suggests that the natural concentration of organic material present would be on the order of 0.6 to 2% of the natural organic concentration.

Tolerance of animal to oil

It is assumed that the presence of oil droplets will not impair the animal or change its behavior. The time necessary for generation of oil droplets is considered sufficient for the toxic aromatic compounds to evaporate. Dissolved compounds are considered also not to impair or affect the animal. Uptake of dissolved compounds is not discussed in the model; if it occurs, it will add to the mass of predicted oil transfer.

Metabolic capacity

It is assumed that all oil ingested as oil droplets is excreted. Oil spill observations and experiments do not show metabolism of oil droplets (Conover, 1971; Parker *et al.*, 1970; Maurer, 1977; Spooner and Corkett, 1974). Experiments with oil uptake are generally performed using soluble aromatic fractions which would not be present in weathered oil droplets. The ability of copepods to metabolize the compounds

present in oil droplets has received little attention. It is possible that a compound present in the droplet may be selectively absorbed. Such selective absorption would not significantly change the weights computed by the model equations, although the physiological consequences may be significant.

Non-droplet ingestion

There has not been much quantitative work done on the amount of oil which would adhere to the surface of phytoplankton or organic particles present in the water. The external covering of some phytoplankton contains mucopolysaccarides which would not be hydrocarbon soluble (Hopkins, 1967). Whether the silaceous tests of diatoms would attract an oil film is not known, but many diatom tests are quite irregular in surface. Work by Malinky (1979) on aromatic adsorption to suspended particulates did not find transport by that mechanism to be nearly as important as other pathways. However, weathered crude oil may behave differently. The potential contribution of adhering oil would act to increase the importance of the calculations, and therefore is not considered in the model.

Population density

Population density is a factor in the transfer of oil into fecal pellets in that the more animals, the greater the absolute amount of oil that may be ingested. Copepod population density may vary by an order of magnitude between winter and summer in temperate and arctic

waters. Arctic winter populations are typically extremely low. Species composition, age groups, and sexual differences will all also affect ingestion rates, but these differences are ignored as a first approximation for model calculations. The figures used for population density are assumed to represent a population of uniform individuals.

Food particles

To simplify model calculations, measurements of the carbon biomass resulting from primary productivity are assumed to be produced by uniform cells, ignoring differences in composition and individual cells which would act to influence feeding behavior.

Feces from oil-fed copepods

It is assumed that the fecal material production rate is equal to that of copepods feeding on unoiled systems. At very high oil exposures, copepods have been observed to change fecal pellet production rates. Spooner and Corkett (1974) observed a "markedly slower rate" of pellet production in 10 ppm oil compared with that in 2 ppm or in the control. Ustach (1977) exposed an estuarine harpacticoid copepod, *Nitocra affinis*, to the soluble fraction from 200 µl oil l^{-1}. He did not observe any reduction in filtering rates but did observe a significant decrease from the controls in fecal material production. Oil levels used in model calculations are generally low enough that reductions in fecal production rates would not be expected. Further information contained in the literature on fecal pellets and their production is cited in Appendix III.

Pellet density

The density of the pellet, and its total mass, is the critical factor in determining the importance of each individual pellet in rapid transit to depths (McCave, 1975). If the inclusion of oil in a fecal pellet acts to lighten its density so that it remains in the feeding layer or even rises; it is no longer of interest as a nutrient transfer mechanism in this model.

The density of an oil laden fecal pellet is due to three components, the weight of oil, the weight of unassimilated food, and mineral material from sediment or phytoplankton tests ingestion; divided by the volume.

Referring to Appendix Table II.3, it may be seen that the specific gravity of crude oil is equal to about 1.00. (This figure may vary significantly depending on the particular oil.) The heavier fractions of petroleum are those that would be viscous enough to resist evaporation and other dispersal mechanisms enough to form droplets. Therefore, it may be assumed that the inclusion of oil within fecal pellets will not lighten the pellet density to less than that of seawater (density 1.05). Without experimental data on the production of fecal pellets after exposure to oil, it would be foolish to attempt to guess the number and volumes of pellets contained in a population's fecal mass, or to calculate a Stokes or other appropriate settling velocity. Therefore, this topic of pellet density, as shown by attempts to include it in the model, is critical to further studies attempting to establish the importance of fecal pellets in oil transport. Until settling

velocities may be calculated, discussion of Phase 4 or the further fate of the pellets is nebulous. If settling velocities are too slow the pellets will not reach the benthos, but will be recycled in upper layers of the water column. A discussion of sediment transport processes is contained in Appendix IV.

Non-limited Ingestion Equations

For the purposes of the model, changes in the rate of ingestion and average ingestion for the population over the course of the day are ignored. It is assumed that the animals have a preferred daily ration and feeding patterns are adjusted to permit ingestion of that ration (given ambient food concentrations are sufficient). Then, remembering the assumption of non-selective feeding upon mixed concentrations of oil droplets and phytoplankton, the populations metabolic need, P_I, is:

$$D \cdot M = P_I \qquad P_I \leqslant P \tag{1}$$

given a food concentration = P
individual daily ration = M
oil concentration = O
grazer population = D

the amount of oil which would be ingested, O_I, during satisfaction of the metabolic need is:

$$O(P)^{-1} \cdot P_I = O_I \tag{2}$$

where P has units of weight of carbon (C) (plant) volume^{-1}

M has units of weight C individual^{-1} day^{-1}

O has units of weight oil C volume^{-1}

D has units of individual volume^{-1}

P_I has units of weight plant C ingested volume^{-1} day^{-1}

O_I has units of weight oil C ingested volume^{-1} day^{-1}

The clearing rate necessary to achieve the daily ration at that food concentration may be calculated by dividing M by P. It is important to do this in order to insure that the assumed daily ration is obtainable at the stated ambient food concentration. Appendix Table I.1 may then be referred to for rates the animals are able to maintain.

Model calculations are made assuming that the numbers given for phytoplankton and oil droplet concentration refer not only to the weight of carbon and the weight of oil droplets, respectively, per volume, but also to numbers per volume. Thus, the fractional value of the oil mass to the food mass also equals the fraction of oil droplets to food cells. A given weight of phytoplankton carbon may reflect very different numbers of cells, depending on the phytoplankter species present, but it is necessary to assume that the oil droplets are close to the phytoplankters in dimension and weight in order for the feeding behavior not to be selectively skewed. If the oil droplet concentration differs in dimensions from the phytoplankton cells, it is likely that the animals will soon learn to select against the oil droplets. From the comparison of oil droplets to phytoplankters given in Appendix I, it may be seen that oil droplets can exist in similar dimensions and masses as phytoplankton cells. It is obviously an idealization to assume all the oil droplets generated after an oil spill will closely resemble the ambient phytoplankton. However, it seems likely that only the droplets which do will be fed upon. Therefore, model calculations are made for this

idealized situation in order to evaluate the greatest potential mass transfer given favorable conditions.

Maximum daily ration and the capacity of the animal to ingest oil

It is assumed in this model that the copepod will feed until it ingests the daily ration necessary for maintenance. The oil droplets ingested during this search will move through the digestive system and be excreted. However, if the availability of oil droplets is much greater than that of the food, the animal could ingest a total organic content much greater than the amount normally processed. There must be some sort of physiological limit to ingestion determined by the capacity of the digestive organs and speed in processing. Therefore, it is assumed in this model that the total ingested material may not exceed twice the maximum daily ration. For further discussion of this topic, see Appendix I.

The need for an ingestion limit

Parker *et al.* (1970) propose that a population of *Calanus finmarchicus* of 2,000 individuals m^{-3}, each with a clearing rate of 100 ml day^{-1} and fecal pellet production of 300 day^{-1} would immobilize 0.3 g oil m^{-3} day^{-1}, with an oil content per pellet of $0.5 \cdot 10^{-6}$ g. He goes on to propose that the concentration of oil in the water column which would provide the maximum rate for oil immobilization by this route as 1.5 ppm. Apparently, the calculation of this oil concentration was made by first calculating from the maximum values reported in the

literature for fecal production and fecal pellet weight a maximum possible oil immobilization in fecal pellets. Dividing that number by the population density times the clearing rate (again a maximum assumed from literature values) provides the oil concentration necessary to permit this immobilization rate.

The problem with this approach is that it may lead to estimations of an optimum oil concentration which are probably far beyond the ability of the organism to tolerate. Calculations using the high range of published fecal pellet dimensions and production would lead to estimations greater than 50 ppm.

Upper-limited ingestion equations

The population of grazers (D) times the maximum weight of organics that individuals are able to ingest in a given unit of time (2M by assumption) results in the calculation of a maximum utilizable organic weight (G_{I_M}) for that population over a given time span.

$$D \cdot 2M = G_{I_M} \tag{3}$$

In order to determine the concentration of organics in the water which would permit feeding to that extent, it is necessary to consider the volume of water that population can filter in that time period. Dividing G_{I_M} by the population density (D) times the clearing rate (C) thus results in the calculation of the optimal organic concentration in the water for feeding (G_M).

$$G_M = G_{I_M} (D \cdot C)^{-1} \tag{4}$$

It is considered that the animal will feed until it has ingested its maximum daily ration disregarding non-assimilable oil particles ingested in the process. It is also assumed that the animal will not be able to contain or process more than twice the amount of organic matter it normally ingests. Therefore, 2M is the upper limit of ingestion of organic matter per individual. It then follows the optimum oil concentration (O_M) for transfer can be no more than half of the previously calculated optimal organic concentration (G_M).

$$O_M = 0.5\ G_M \tag{5}$$

At oil concentrations higher than O_M the animal will be forced to stop feeding before it has ingested its daily ration due to physiological limitations. The further assumption is thus that the animal is able to sense, when feeding at oil concentrations too high to permit ingestion of the daily ration, that too large a portion of its ingested particles is unusable, and will cease to feed. This assumption is somewhat supported by the work of Reeve and Walter (1977) who studied the feeding of copepods in the presence of sand particles. Further work is needed to determine exactly how sensitive the animals are to the metabolic value of their food and how the mechanism of this sense functions.

Thus, equation (1) is subject to the further limit that:

$$P_I \leq 0.5\ G_{I_M}$$

and equation (2) is subject to the further limit that:

if O>P the animals will cease to feed.

Lower limit to model calculations

Frost (1975) reports that at low food concentrations copepods will significantly reduce their filtering rates. If the animals cease feeding this forms the theoretical lower limit to the model of zero ingestion, since the animal is unable to obtain its daily ration within its filtering capabilities. However, this threshold food concentration has not been widely reported and in the context of the model the daily ration is set at a figure representing what is thought to be the animals normal intake in the particular environmental conditions studied. Thus, the volume chosen for daily ration is the working limit to ingestion in the model.

Equations Predicting the Transport of Oil into Fecal Pellets

Given the assumptions discussed in the preceding sections, the fecal mass (F) produced by the grazer population equals the oil ingested (O_I) plus the fraction (n) of ingested food material (P_I) not assimilated. Calculations will be performed over the range of possible assimilation efficiencies.

$$F = n(P_I) + O_I \tag{6}$$

F = fraction of total ingested material excreted by population (weight time^{-1} volume^{-1})

n = fraction of food not assimilated.

CHAPTER 3

MODEL RESULTS

This chapter demonstrates the application of the model equations towards prediction of potential oil transport by fecal pellets. Specific sites in Alaskan waters: Port Valdez and the southeastern Bering Sea; were selected as example test sites. A fairly good data set exists for these areas. I have included in Appendix V a baseline hydrocarbon analysis of plankton samples from the Bering Sea. Port Valdez, due to its position as the terminus of the Trans-Alaskan pipeline, has a great deal of tanker traffic and a continual low-level input of oil due to the ballast-water treatment plant. Thus, the fate of oil spilled in Port Valdez is of great interest. The southeastern Bering Sea is of great importance to commercial fishermen and crabbers. It is a highly productive area. If leasing of oil tracts in the Beaufort Sea or other northern areas is continued, the Bering Sea may become subject to tanker traffic also.

Following quantitative predictions of the mass of oil which may be transferred into zooplankton fecal pellets, in these areas, the discussion will include ideas as to the possible future of this oil and potential for impact to other organisms.

Transfer of oil through the food web may occur through two different pathways. The first is predation upon copepods containing oil. The second is *via* ingestion of fecal pellets containing oil. The first pathway is not the topic of this thesis and will not be discussed. The second pathway will be discussed without quantitative prediction. Exposure to

contaminated fecal pellets will depend upon the movements of the water mass containing the oil and copepods. The water depth and pellet density will determine whether the pellets are more likely to reach the benthos or bathypelagic organisms.

Basic Simulations

Physical description of sites

The southeastern Bering Sea

The southeastern Bering Sea, or outer Bristol Bay, is presently the site of the "PROBES" (Productivity and Resources of the Bering Ecosystem) project, a multi-institutional investigation of primary productivity processes. The Bering Sea lies over a relatively shallow and one of the world's widest continental shelf. From PROBES data, it has been found that the area contains two different water masses or physical regimes, with fronts (defined as zones, approximately 25-50 km wide, of reduced horizontal fluxes of properties) where different water masses meet (Coachman, 1978). The outer or shelf break front is centered over the shelf break and continental slope, and the inner front is centered more than 400 km inshore along the 100 m isobath. Shelf water fills the large central area of greater Bristol Bay between (approximately) the 50 to 100 m isobaths. There is little salinity stratification in this area and in winter little temperature stratification. In the summer a warm surface layer extends to about 20 m. There appear to be significant year-to-year variations in the characteristics of the shelf water, mainly due to the meteorological conditions of the preceding

winters. Water temperatures during the summer may vary from -1 to 3.5°C (Coachman, 1978). The central shelf area appears to be a system where primary production fuels the benthic system (Cooney *et al.*, 1978).

The outer front extends almost continuously along the edge of the entire eastern Bering Sea shelf, in the upper 60 to 80 m of the water column. Waters have a relatively long residence on the outer shelf, drifting towards the northeast at about 1 cm sec^{-1}, parallel to the bathymetry. At any time, tidal water motions may be as rapid as 1 knot, however. The source water mass for the outer shelf regime on the seaward side is the Alaska Stream. The water is quite warm (3-4°C) at deeper shelf depths. The lateral, or on-off shelf, flux of water properties is basically tidal driven (Coachman, 1978). The outer shelf seems to be mainly a pelagic system, with primary production feeding pelagic copepods and fishes (Cooney *et al.*, 1978).

Phytoplankton productivity in the outer shelf break front region was generally found to be greater than at the inner shelf front region, in 1978. Chlorophyll *a* values were very low in waters adjacent to the Aleutian Chain. Chlorophyll *a* values in the PROBES study area in 1978 ranged from less than 1 mg m^{-3} to 15 mg m^{-3} (Goering and Iverson, 1978). Copepod levels ranged from 100 to 450 animals m^{-3} (Cooney *et al.*, 1978).

From this information, it appears that the central shelf area would be more sensitive to a rapid transit of oil to the benthos than would be the outer shelf area, the more pelagic system. Meteorological conditions and the seasonal timing of the pollutant input would also affect the severity of impact, or whether there would be any interactions with sea ice.

This thesis has not gone in depth into the prediction of oil spill trajectories, nor are detailed predictions possible with the present state of knowledge. Oil spills are generally thought to move at a velocity equal to the current velocity or at a velocity 1-3% of the wind velocity (Waldman *et al.*, 1973). From the table listing physical descriptions of Alaskan waters (Appendix Table II.4), it is possible to make some general suggestions about the future of an oil spill in the Bering Sea. The spill would move in the direction of the prevailing current, thus it would travel counterclockwise from the spill point, averaging about 2 cm sec^{-1}, neglecting wind effects which could increase its speed. The volume of the initial spill, and the amount of mixing energy provided by turbulence, would determine the concentration of oil distributed within the water column. Transport northward in the south Bering Sea has been calculated at 14 Sv (Sv - Sverdrup, 10^6 m^3 sec^{-1}, a measure of transport; Favorite, 1972).

Port Valdez

Port Valdez is a glacial fjord located in the north portion of Prince William Sound. Residence times of waters within Port Valdez average 40 days. There is no constant circulation pattern of the waters in the bay but the net water motion at depth is from the Jackson Point region toward the head of Port Valdez. Winds have great importance in forcing currents. Maximum winds in winter may be 20 knots with 80 knot gusts. Easterly winds are common in the winter and force a regular westward movement of water at 15 m. In the summer the

circulation at 15 m is primarily tidal-driven with some transient wind-driven influences. The circulation from river runoff is restricted to the upper 10-15 m of the water column. Currents up to 1 knot have been measured at the 15 m depth. At the Valdez Narrows the current maximum is 20 cm sec^{-1}, and the usual velocity of inflowing water is 2 to 3 cm sec^{-1}. Tides are mixed and semi-diurnal (Muench and Nebert, 1973). Annual net primary production is approximately 200 g C m^{-2} yr^{-1} in Valdez Arm and about 150 g C m^{-2} yr^{-1} in Port Valdez (Goering *et al.*, 1973). Summer levels of copepods average 2,000 individuals m^{-3} (Damkaer, 1976).

The diffuser releasing the water from the ballast water treatment plant has a hydrocarbon level of 8 ppm. Hood *et al.* (1973), considering dilution rates, predict that the maximum hydrocarbon concentration in Port Valdez waters will be 44 ppb. There is also potential for a large oil spill resulting from tanker traffic. The trajectory of an oil spill in Port Valdez is especially difficult to predict since circulation patterns are often wind forced.

Variable selection considering environmental conditions

The actual variables used in model calculations are the phytoplankton and copepod concentrations in the water, the maximum daily ration desired by the animals, and their fecal production rate or assimilation efficiency. Other environmental conditions act to influence these variables and also the fate of oil hydrocarbons introduced into the water. These conditions include the water temperature, storm patterns,

the wind and current regime; all influenced, of course, by the time of year.

Over the course of the year, the phytoplankton concentration (and composition) waxes and wanes depending upon available nutrients and light. In turn the copepod concentration (and composition) will reflect the availability of food. As indicated in Chapter 2 and Appendix I, the phytoplankton concentration will not only affect the size of the zooplankton population but will also determine feeding behavior, and oil ingestion. Different herbivorous copepod species vary in the lag time with which a bloom of animals follows the bloom in their food supply. Animals may be grouped with regard to this timing of over-wintering and reproductive strategy. Some species time the population and juvenile bloom to occur concurrently with the plant bloom. Other species delay their bloom (Zenkevitch, 1963). Given a model situation such that the bloom was concurrent, conditions would perhaps be optimum for oil transfer, since oil levels are less likely to deter feeding if food particles are also present in good quality, and animal density would be high and would increase the mass ingested. Spring bloom conditions, and summer conditions for some zooplankters, may be viewed as population extremes and winter levels as extreme lows. However, the time scale with which spring bloom conditions are evaluated must be small enough to discern whether differences in bloom timing will sway model predictions significantly.

Assimilation efficiency will be less in conditions of high food concentrations than in low (Steele, 1974), thus spring bloom would again be a time promoting oil transfer into fecal pellets.

Metabolic rations might be expected to decrease with decreasing temperature, but also to increase near reproduction (Steele, 1974). Therefore, it is difficult to know whether there will be a change throughout the year significant to model calculations, and in what direction the change will act.

The change in physical characteristics from "winter" conditions to those of spring bloom may not be as significant for the model simulation as the biological extremes. Extremes in physical characteristics are found between winter, even spring bloom, conditions; where water temperature is low, winds and storms high, promoting creation, mixing, and durability of oil droplets; and summer conditions of calm weather and high temperatures. Thus, summer might be a time when the percentage of droplets transferred from the total present is high, since population densities will still be much higher than winter lows; and less droplets would be created from a spill of given tonnage.

From the foregoing it appears the winter conditions would be the least favorable for significant oil transfer into fecal pellets. Winter conditions also increase the potential toxicity of an oil spill to the copepods. An additional stress to overwintering animals at this time is critical, since it may impair reproduction and thus species survival.

Limiting assumptions

In model simulations a given mass of oil in the form of droplets identical to the ambient phytoplankton is postulated to be generated from a surface oil spill. The mass flux of the oil into animals, and

into fecal pellets, will be calculated on a time-scale of 1 day. Variations in model parameters within that time will be averaged for the day. Food concentrations and oil droplet concentrations will be treated as constant during that period, ignoring the decrease due to feeding. Vertical mixing processes occurring within that period are also ignored. At some sites the presence of vertically migrating species of copepods will be treated by choosing the population density figure to represent the maximum density present in the layer over the course of the day. The time frame of model simulations relative to an oil spill is assumed to be 48 hours past the spill, in order for toxic compounds to evaporate and for oil droplets to be generated. Thus, a significant portion of total released oil has already undergone transport via different routes than the one discussed here.

Results

Predicted values

The format for calculation and display of results is to assume certain maximum values for the food and zooplankton concentrations, the daily ration, and the oil concentration. Variations in the first three would be expected to be seasonally dependent. Therefore, each simulation examines the changes from maxima across the year. The changes in variable levels across the year considered likely are shown in Table 3. The background information given in previous portions of this paper and in the appendices should explain these assumed patterns. Tables 3 and 4 present predicted values for the Bering Sea and Port Valdez using model equations.

TABLE 3. Input variables.

Season	P [food]	D zoop. density	O [oil]	n Fraction not assimilated	M daily ration
spring bloom (A)	high	lag	high	high	high
spring bloom (B)	high	high	high	high	medium
summer	medium	high	low	medium	medium
winter	low	low	high	low	low

TABLE 3. Continued.

Terms and Symbols

Input Variables	Symbol	Units
oil droplet level	O	mg oil m^{-3}
animal density	D	individuals m^{-3}
food density	P	mg C m^{-3}
fraction not assimilated	n	none
maximum daily ration	M	µg individual^{-1} day^{-1}
winter	W	
summer	S	
spring bloom A lag in zooplankton reproduction	A	
spring bloom B no lag in zooplankton reproduction	B	

Predicted Variables

Terms	Symbol	Units
clearing rate	C	ml individual^{-1} day^{-1}
food ingested	P_I	mg C day^{-1} m^{-3}
oil ingested	O_I	mg oil day^{-1} m^{-3}
fecal mass	F	mg day^{-1} m^{-3}
increase in fecal mass due to oil content	FX	none
transfer of oil into individuals relative to initial oil mass	O_I/O	none

TABLE 4. S. Bering Predictions. Refer to Table 3 for symbol and unit explanation.

Simulation A

	Input					Output					
	P	O	M	D	n	C	P_I	O_I	F	FX	$\frac{O_I}{O}$
High Levels											
Spring bloom A	500	500	10	500	0.5	20	5	5	8	3	0.01
bloom B	500	500	6	2500	0.5	10	20	20	30	3	0.04
Summer	200	200	6	2000	0.4	30	10	10	10	3	0.05
Winter	100	500	5	500	0.3	50	NF	0	0.0	0.0	0.00
Low Levels											
Spring bloom A	500	100	10	500	0.5	20	5	1	4	1	0.01
bloom B	500	100	6	2500	0.5	10	20	4	10	1	0.04
Summer	200	20	6	2000	0.4	30	20	1	10	1	0.05
Winter	100	100	5	500	0.3	50	3	3	4	4	0.03

TABLE 4. Continued: S. Bering Predictions.

Simulation B

	Input					Output					
	P	O	M	D	n	C	P_I	O_I	F	FX	$\frac{O_I}{O}$
High Levels											
Spring bloom A	500	500	100	500	0.5	200	50	50	80	3.0	0.1
bloom B	500	500	60	2500	0.5	100	200	200	300	3.0	0.4
Summer	200	200	60	2000	0.4	300	100	100	200	4.0	0.5
Winter	100	500	50	500	0.3	500	NF	0	0	0	0.0
Low Levels											
Spring bloom A	500	100	100	500	0.5	200	50	10	40	1	0.1
bloom B	500	100	60	2500	0.5	100	200	40	100	1	0.4
Summer	200	20	60	2000	0.4	300	100	10	50	1	0.5
Winter	100	100	40	500	0.3	400	20	20	30	4	0.2

TABLE 4. Continued: S. Bering Predictions.

Simulation C

	Input					Output					
	P	O	M	D	n	C	P_I	O_I	F	FX	$\frac{O_I}{O}$
High Levels											
Spring bloom A	15	15	4	500	0.5	300	2	2	3	3.0	0.1
bloom B	15	15	3	2500	0.5	200	8	8	10	3.0	0.5
Summer	10	10	3	2000	0.4	300	6	6	8	4	0.6
Winter	5	5	2	500	0.3	400	1	1	1	4	0.2
Low Levels											
Spring bloom A	15	5	4	500	0.5	300	2	0.7	2	2	0.1
bloom B	15	5	3	2500	0.5	200	8	3	7	2	0.6
Summer	10	2	3	2000	0.4	300	6	1	4	2	0.5
Winter	5	5	2	500	0.3	400	1	1	1	4	0.2

TABLE 4. Continued: S. Bering Predictions.

Simulation D

	Input					Output					
	P	O	M	D	n	C	P_I	O_I	F	FX	$\frac{O_I}{O}$
High Levels											
Spring bloom A	500	500	100	50	0.5	200	5	5	8	3	0.01
bloom B	500	500	60	400	0.5	120	20	20	30	3	0.05
Summer	200	200	60	200	0.4	300	10	10	20	4	0.05
Winter	100	500	50	50	0.3	500	NF	NF	0.0	0.0	0.0
Low Levels											
Spring bloom A	500	100	100	50	0.5	200	5	1	4	1	0.01
bloom B	500	100	60	400	0.5	100	20	5	20	2	0.05
Summer	200	20	60	200	0.4	300	10	1	6	1	0.05
Winter	100	100	50	50	0.3	500	3	3	4	4	0.03

NF = prediction for feeding cessation.

The simulations are paired. In each pair the density of food and animals, and the maximum daily ration values remain constant. The effect of the oil concentration is then studied from a level only a fraction (generally one-tenth) of the food concentration to a level equal to the food concentration. At each season it is assumed that the oil droplets are generated from a spill of the same magnitude but summer levels are set arbitrarily lower to reflect the assumption that physical conditions at this season would promote less droplet formation.

In each simulation the effect of timing of the copepod bloom during the spring phytoplankton bloom is calculated (spring bloom A and B). The value given for oil ingestion (O_I), as explained in Chapter 2, is assumed to equal that oil excreted. Thus, the excreted matter (F) is the total mass of oil-contaminated fecal material the population produces. The "FX" column gives the increase in fecal mass caused by the oil droplets over what would be expected in the unpolluted situation. The ratio of the ingested oil to the initial oil (O_I/O) droplet concentration shows the percentage of oil transferred into fecal pellets.

In Table 4, Simulation A uses food values (500 mg m^{-3}) in the range reported by Alexander (1976) for the south Bering Sea; zooplankton levels near that reported by Zenkevitch (1963), and daily ration values in the lower range of those given in the literature. Simulation B follows the above, except in using somewhat higher daily ration values. Simulation C uses food values at an extremely low level, an oil spill of smaller magnitude, and very low daily ration values. Simulation D follows B but examines the effect of lower zooplankton densities, in the low range seen by Cooney *et al.* (1978).

Table 5 reports predicted values for Port Valdez. Simulation A postulates in one case an oil level equal to the 44 ppb dilution predicted by Hood *et al.* (1973) and an equal mass of phytoplankters; with a lower oil level in the second case. Daily rations are low, and population densities in the range found by Damkaer (1976). Simulation B sets the phytoplankton composition near that found by Larrance (1976) with daily rations assumed somewhat higher, and the same population density of animals.

The figures given in these tables are calculated as an example of the application of the model equations. They are not intended to be definitive predictions for these areas, but they do illustrate a range of real possibilities. If more data were available, one could apply a computer program to actual station-by-station data on zooplankton density and composition and primary productivity values. The assumption for the desired daily ration could then be keyed to the zooplankton species present and the time of year. Such a station-by-station procedure applied to the PROBES data might quantify the differences between the inner and outer front regimes postulated in the first section of this chapter. A sufficiently elaborate program could subgroup the populations metabolic need (P_I) by zooplankton species and age groups present, and then sum the total need for the grazer population. Such a technique would lessen the error introduced here of treating the zooplankton population as being composed of uniform members.

TABLE 5. Port Valdez Predictions. Refer to Table 3 for symbol and unit explanation.

Simulation A

	Input					Output					
	P	O	M	D	n	C	P_I	O_I	F	FX	$\frac{O_I}{O}$
High Levels											
Spring bloom A	44	44	10	500	0.5	200	5	5	8	3	0.1
bloom B	44	44	6	2000	0.5	100	10	10	20	3	0.2
Summer	40	20	6	1000	0.4	200	6	3	5	2	0.2
Winter	20	44	5	500	0.3	300	NF	NF	NF	0.0	0.0
Low Levels											
Spring bloom A	44	10	10	500	0.5	200	5	1	4	1	0.1
bloom B	44	10	6	2000	0.5	100	10	3	8	2	0.3
Summer	40	5	6	1000	0.4	200	6	0.8	3	1	0.2
Winter	20	10	5	500	0.3	300	3	1	2.0	2	0.1

TABLE 5. Continued. Port Valdez Predictions.

Simulation B

	Input					Output					
	P	O	M	D	n	C	P_I	O_I	F	FX	$\frac{O_I}{O}$
High Levels											
Spring bloom A	300	300	40	500	0.5	100	20	20	30	3	0.06
bloom B	300	300	30	2000	0.5	100	60	60	100	3	0.2
Summer	200	200	30	1000	0.4	200	30	30	40	4	0.2
Winter	50	300	20	500	0.3	400	NF	NF	0	0	0.0
Low Levels											
Spring bloom A	300	44	40	500	0.5	100	20	3	10	1	0.06
bloom B	300	44	30	2000	0.5	100	60	8	40	1	0.2
Summer	200	20	30	1000	0.4	200	30	3	20	1	0.2
Winter	50	44	20	500	0.3	400	10	8	10	4	0.2

NF = prediction of feeding cessation.

Discussion

The effect of variable choice on the simulations

The southeastern Bering Sea

Predictions of transfer in the south Bering Sea range from zero to 200 mg m^{-3} day^{-1}. The percentage of the initial oil droplet concentration transferred thus into fecal pellets ranges from zero to 60% on the first day. The amount of oil ingested reflects the assumptions for copepod density and maximum daily ration. The higher the choice of values for these variables, the higher the predicted value for oil ingestion. Thus, spring bloom and summer conditions permit the best opportunities for maximum transfer. The concentration of phytoplankton limits transfer in that, if the concentration of initial oil droplets exceeds that of the phytoplankton, by assumption there will be no feeding and thus no transfer. Therefore, the lower the phytoplankton concentration the less potential transfer and the more stress upon the grazing population. The inclusion of oil in the excreted material ranges from slightly increasing the mass of excreted material to quadrupling it.

Port Valdez

Predictions for transfer in Port Valdez range from zero to 60 mg m^{-3} day^{-1}. The percentage of the initial oil droplet concentration transferred into fecal pellets ranges from zero to 30% on the first day. The inclusion of oil in the excreted material again ranges from slightly increasing the mass of fecal material to quadrupling it. The effect of the choice of variables is the same as those discussed for the Bering Sea.

Comparison with recent PROBES data

Recent data has shown both primary productivity and herbivore ingestion to be higher than expected, at least for the outer front. Cooney and Coyle (1981) report that outer shelf herbivores harvest 1.4 g C m^{-2} day^{-1} and middle front animals 0.2 g C m^{-2} day^{-1}, at maximum. To apply these figures in terms of the model, postulating an oil spill which produced oil droplets resembling the ambient phytoplankton, outer front herbivores may ingest 1.4 g C m^{-2} day^{-1} of food plus 1.4 g oil m^{-2} day^{-1}. The fecal matter then released, given the fraction not assimilated as 0.3, would have a weight of 1.8 g m^{-2} day^{-1}. Middle front animals, correspondingly, might ingest 0.2 g oil m^{-2} day^{-1} and excrete a mass of 0.3 g m^{-2} day^{-1}. Cooney and Coyle (1981) also report that middle front herbivores are much smaller than the pelagic species found at the outer front and that the small herbivores display a lag in reproduction from the time of spring bloom. Thus, while the middle front is a benthic system, fecal pellets would not be an important transfer mechanism here. Pellets produced by small animals would not be expected to be dense enough to sink to great depths. The lag in reproduction indicates that too few animals are present for much oil ingestion at the time when food concentrations are high enough to permit continued feeding. Any contribution fecal pellets did make to organic loading on the sediments would be far outweighed by the ungrazed settling phytoplankton.

The significance of oil transfer

Relative to the initial mass of the oil spill

For the south Bering Sea the percentage of oil transferred into fecal pellets from the initial concentration of oil droplets ranges from zero to 60% on the first day. For Port Valdez, the percentage ranges from zero to 30%. Thus, given the right conditions, a significant portion of the initial suspended oil droplets may be removed from the water column by copepod feeding. Continued over several days, total or near-total removal of the oil droplets could occur. However, it is important to remember that the time frame of the model is assumed to be 48 hours after the spill. Thus, a considerable portion of the oil has already undergone degradation through other pathways. As discussed in Appendix II, evaporation alone may remove 50% of the hydrocarbons from an oil spill. So, maximum removal of the oil spill via copepod grazing could act upon perhaps 30% of the initial oil mass, and would take at least 2 days. This ignores possible additional ingestion of oil during the first two days after the spill which are not covered by model calculations for reasons previously stated. If such ingestion were to occur, it would increase the calculated transport.

Also, model calculations are made for an idealized case in which all oil droplets generated from the spill closely resemble the ambient phytoplankton. Since, in the real situation there are likely to be many droplets which are not similar, grazing mechanisms will not remove as many droplets as predicted.

To the grazers

From Table 4 it may be seen that highest oil ingestion occurs in the southeastern Bering Sea when the grazer population is high, and the desired daily ration high. This also depends on a high phytoplankton population in order to maintain the animals feeding behavior. Thus, summer months have high rates of transfer, and a spring bloom occurring concurrently in phytoplankters and zooplankters presents high potential for oil transfer into fecal pellets. In this spring bloom situation the juveniles may be more susceptible to the oil exposure than in the summer when they have matured somewhat. In a spring bloom in which a lag occurs between the timing of the phytoplankton bloom and the grazer bloom, the oil exposure may again jeopardize success of grazer reproduction. Due to the low grazer population, this situation also does not present a high potential for oil transfer. In an oil spill of great magnitude, if the concentration of oil droplets was such that the animals ceased feeding, the juveniles would not have an energy reserve sufficient to survive. In the summer, calmer weather conditions might slow the production of oil droplets but the phytoplankton are also being quickly utilized by the grazers so the possibility of cessation of feeding behavior due to high oil droplet concentrations still remains. During the summer animals are building up energy reserves for the winter so a cessation of feeding might be more deleterious to over-wintering survival than to immediate mortality. Winter months may permit some amount of oil transfer into fecal pellets, but also is the most likely time for oil droplets to outweigh phytoplankters. While the grazing

population probably is not feeding much anyway but living off stored energy reserves, total cessation of feeding and possible contamination of energy reserves may impair the chances of surviving the winter. A quadrupling in fecal mass may be physiologically difficult for the animal and could create added stress.

In Port Valdez, Simulation A phytoplankton levels were assumed equal to the dilution rate predicted by Hood *et al.* (1973). This phytoplankton level is much lower than that found by Larrance in 1976. In the simulation oil transfer is low, with spring bloom with no zooplankton lag providing the best opportunity. In winter a cessation of feeding is predicted. In Simulation B a more probable phytoplankton level is assumed. In the high oil calculation set an oil level equal to the phytoplankton is assumed, such as might occur after a tanker spill. Here, oil transfer is more sizable, and a cessation of feeding is again predicted in winter months. In the low oil calculation set the chronic oil level predicted by Hood *et al.* (1973) is again assumed. This calculation set is perhaps closest to the most likely situation. The mass of oil transferred is predicted to be small, with winter months providing the best opportunity. Much of what was said in the preceding discussion of the south Bering Sea will apply to Port Valdez. Quite clearly winter months are the critical period in Port Valdez.

Potential impact on the food web

Phase 4 or transfer of oil through the food web may occur via predation upon copepods containing oil or via ingestion of fecal pellets

containing oil. It is beyond the scope of this project to discuss Phase 4 in detail, but it is possible to make some projections based on the information included here. The purpose for doing this is to indicate areas that deserve further study. A second reason for including these suggestions is to relate the impact of oil ingestion within the copepods behavior to the wider ecological system of which the copepod is a part. It is hoped that the reader will begin to sense the many factors that will influence the path of the oil in the days following the spill.

As the spill moves along, the main water mass containing the oil might be viewed as a microcosm in which copepods would be exposed to an oil droplet concentration that would be subject to their degradation. As the mass is transported, underlying benthos would be subject to falling oil particles within fecal pellets. Away from the center of the oil mass the concentration of oil droplets would steadily decrease.

Food web transfer may occur via Phase 2; in other words, by predations upon contaminated individuals. By this means mobile predators, who could have some ability to avoid contaminated waters, may become contaminated by a school of zooplankton in waters which seem to have a low pollutant concentration. For the south Bering Sea an O_I is calculated for the population of 0.2 g m^{-3} day^{-1} maximum, with smaller values predicted in Port Valdez. Per copepod, this would be 60 µg (30 in Port Valdez) ingested during the day. Since the animals excrete often, they may contain perhaps 1 µg at any time. A juvenile fish eating 100 copepods per day would ingest 0.1 mg oil, and 0.05 mg oil maximum in Port Valdez. Juvenile fish have been shown to be sensitive

to oil in the surrounding water at a concentration of 0.1 ppm (Moore and Dwyer, 1974). The effect of actually ingesting 0.1 mg of weathered oil is not certain. Ctenophores, an important copepod predator, when exposed to napthalene concentrations of 160 mg m^{-3} had a high mortality rate. Napthalene concentrations within the ctenophores were measured at 40 µg per g dry weight of the animal (Lee and Anderson, 1977). Levels predicted here may approach 100 µg per fish (which weigh perhaps 1 g wet weight). Napthalene is one of the most toxic compounds in oil and would have serious effects at lower concentrations than other compounds. It would not be expected to be present in weathered oil droplets. Further discussions of the effect of oil on plankton and fish can be found in Appendices I and II.

The prediction 0.1 mg of crude oil per animal is probably not a large organic input, compared to the biomass also ingested. Since it seems most likely that weathered oil is simply excreted, and the amounts are fairly small, it does not appear that contamination of higher trophic levels will be significant. Perhaps the most serious effect could be caused by selective accumulation of refractory compounds from the droplets, but this has not been studied.

Fecal pellets, as discussed previously, have been shown to be important in nutrient transfer and as a source of food for organisms dwelling deeper in the water column and on the benthos. Maximum assumptions for the south Bering Sea would expose these deep organisms to a concentration of oil of 0.2 g m^{-3} day^{-1}, and 0.06 g m^{-3} day^{-1} in Port Valdez; as long as the contamination of animals and water occurs above.

At maximum, in winter months, a quadrupling in fecal mass due to oil is predicted. Thus, deep organisms would be exposed to oil they might otherwise have escaped.

The amount of fecal matter reaching the sediments depends on the depth and the settling velocity of the pellets. As discussed in Chapter 2, experimental work is needed to make predictions on oiled pellet density. Generally, only a small proportion of a population's fecal matter reaches the sediments (Turner, 1977a). At non-toxic oil levels refractory compounds could enter the food web via ingestion at the benthic boundary, and become concentrated in higher organisms. The food value or possible toxicity of a fecal pellet containing oil is not known. However, since it is assumed that the copepod is able to eat and excrete the oil droplet without great ill effects, it is not likely that higher trophic levels would be affected differently.

Transfer to sediments

The mass of the contaminated pellets may affect physical and microbial degradation processes. Particulate organic carbon suspended in the water column in the Arctic Ocean ranges from 2-14 mg C m^{-3}, and 0.2-1 g C m^{-3} in the Bering and Chukchi Seas (Loder, 1971). The mass of oil-laden fecal pellets predicted at a maximum for the Bering Sea was 0.2 g m^{-3}. The mass contributed by oiled fecal pellets in the Bering Sea would be a small increase.

Hydrocarbons are likely to be particularly resistant to microbial decomposition processes. (Again, for a more detailed discussion of

sediment decomposition, see Appendix IV.) Sediment type will affect decomposition processes but probably not to an extent significant to this discussion with these predicted quantities of loading. It is likely that the oil will not be biologically degraded at the sediment surface. Depending on the sedimentation rate, this could ensure oxygen removal and bring the anoxic layer closer to the surface. The microbial community and the benthos would be altered by the changed conditions. Crabs, and other buried benthos such as clams and burrowing worms, would move to avoid an anoxic environment, most especially if it extended into the water column over the benthos.

The effect of oil-laden fecal pellet sedimentation will be significant only if it causes a rapid change in the rate of sulfate removal, and thus moves the anoxic layer up towards the sediment surface and water column. The hydrocarbons may be fairly resistant to biological transformation. Their burial should act as a barrier to oxygen diffusion. The change in organic substrate caused by the oil could cause a shift in the microbial community, thereby interrupting the usual decompositional sequence. It is impossible to make any definite predictions about these hypothetical effects until more exact measurements of sulfate reduction, carbon loading, and oil transformation rates are available. However, judging from the cases cited in the previous section; the quadrupling in carbon loading due to maximum oil transfer as predicted by the model would be too small to change degradation rates, especially since not all the fecal matter could be expected to reach the sediments.

Comparison of model predictions with baseline hydrocarbon analysis

Appendix V reports baseline hydrocarbon analyses made on Alaskan plankton in order to give an experimental basis for hypotheses concerning the potential toxicity or accumulation of hydrocarbons in the animals.

In the Bering Sea samples, assuming an individual weighs 1 mg wet weight; all samples showed a pristane content of less than 1 µg per individual. Referring to Appendix Table II.1 and taking hydrocarbon content to be 1% of lipid content, the Bering Sea samples appear reasonable. What this suggests in terms of the model run is that oil ingestion could place at any one time a much larger hydrocarbon content in the animals intestinal system than that contained in its metabolic pool. The possibility then exists that there will be some accumulation of hydrocarbons from the intestine into the animal's lipid fraction.

Conclusions

The model predicts that in the Bering Sea a maximum of 200 mg of oil per m^{-3} day^{-1} could be ingested by copepods and excreted into fecal pellets, with amounts somewhat smaller predicted for Port Valdez. This is only a small fraction of the initial oil mass released. The times of year presenting best opportunities for this transfer is the spring bloom with high numbers of phytoplankton and zooplankton, and the summer. Summer months often enable a greater percentage of the initial oil droplets to be ingested (as much as 60% the first day in the Bering Sea) than does the spring bloom situation, given an oil spill of equal magnitude, since summer weather conditions are assumed to generate less oil droplets.

Winter months have greatest chance of serious stress upon the grazing animals due to an oil spill. The low phytoplankton levels in winter months increase the chance of oil droplets outnumbering the food supply to such an extent that the animals will cease to feed. In some of the calculation sets, this was predicted. The increase in fecal matter mass due to the incorporation of oil is greatest in winter, and is predicted to quadruple the biogenic mass. Since not all of the fecal matter will reach the sediments, this is not likely to be a sufficient increase in carbon loading upon the sediments to cause a shift in the anoxic zone.

Model simulations are calculated with maximum masses and numbers of oil droplets being no greater than the maximum carbon mass and numbers of phytoplankton present during the year. It is assumed that any spills generating enough oil droplets to outweigh the phytoplankton will cause the animals to cease feeding. If this assumption is untrue, model calculations underestimate the amount of oil that may be transferred. Evidence for this assumption is discussed in Appendix I.

The importance of this form of biological oil degradation is limited in Arctic waters by the low zooplankton densities common during the winter months. Winter densities change the calculations by an order of magnitude, making the quantity of oil transferred rather insignificant. Winter is also the time when the population is subject to stress and living off stored reserves. The ingestion of oil droplets may affect the quality of the animals lipid reserves. The presence of ice would also act to slow down the normal degradative processes which act on oil.

Low zooplankton densities, coupled with the filtration capacity of the animals, make it apparent that the zooplankters would never be able to come into contact with and clear all oil present in one day. Also, the proportion of oil present as food-sized droplets may be small compared to the total oil present.

The ingestion of oil by grazing copepods could equal the normal ingestion of food. While it is not known to what degree the animals will be able to metabolize crude oil droplets, the processing of these materials will demand energy. This oil could be transferred to higher trophic levels through their predation upon oiled animals.

This model is an attempt to deal with little-understood variables, many of which result from complex feeding interactions. Therefore, the major importance of this model lies not so much in its quantitative predictions, although they do provide an order of magnitude estimation, but in the delineation of the major variables important in this transfer mechanism and the direction of needed future studies.

The conclusion drawn from this model is that any toxic effects which may result from the transfer of oil droplets are likely to result not so much from the quantity but from the energetic costs of transferring the oil (the interference with assimilation efficiency) and the possibility of accumulating refractory compounds. Therefore a biochemical study is needed, perhaps first observing the animals survival and metabolic changes when exposed only to oil droplets, and then the effects when food particles are present.

This thesis has attempted to predict the behavior of copepods in the presence of oil droplets in the light of present understanding of

copepod feeding behavior. Thus, model equations are built upon assumptions which may not be true. Predictions of transfer resulting from the model may in fact be quite wrong. However, construction of the model has served to clarify areas where more research is needed.

Modeling as a technique is subject to the limitations of being a simplified version of the real world. Thus, complex interaction among the parameters is ignored, as is the effect of factors not incorporated in the model. The model imposes artificial constraints and boundaries on the variables, such as the limitations set upon oil droplet size. Data is often inadequate to support the assumptions. The model is an imaginary world, but its simplified structure makes experimentation possible.

The assumption that the animal will be able to ingest a quantity of oil plus its maximum daily ration has no experimental basis. This should be fairly easy to establish by feeding copepods in the presence of oil and food droplets. The assumption that none of the oil droplet is metabolized needs to be examined and tested. The whole interaction of feeding behavior in the presence of oil droplets needs closer examination to see if the animals choose to feed on the droplet, whether there is selective feeding in the presence of droplets, thereby skewing the proportion of oil to food selected, and at what oil levels clearing rates and fecal production rates will change. Experimental values for fecal pellet weights, and production rates, are rarely quoted in the literature, and there is a wide range of reported values.

I believe the fecal transport mechanism is significant, not so much in terms of total oil spill degradation, but in terms of changing

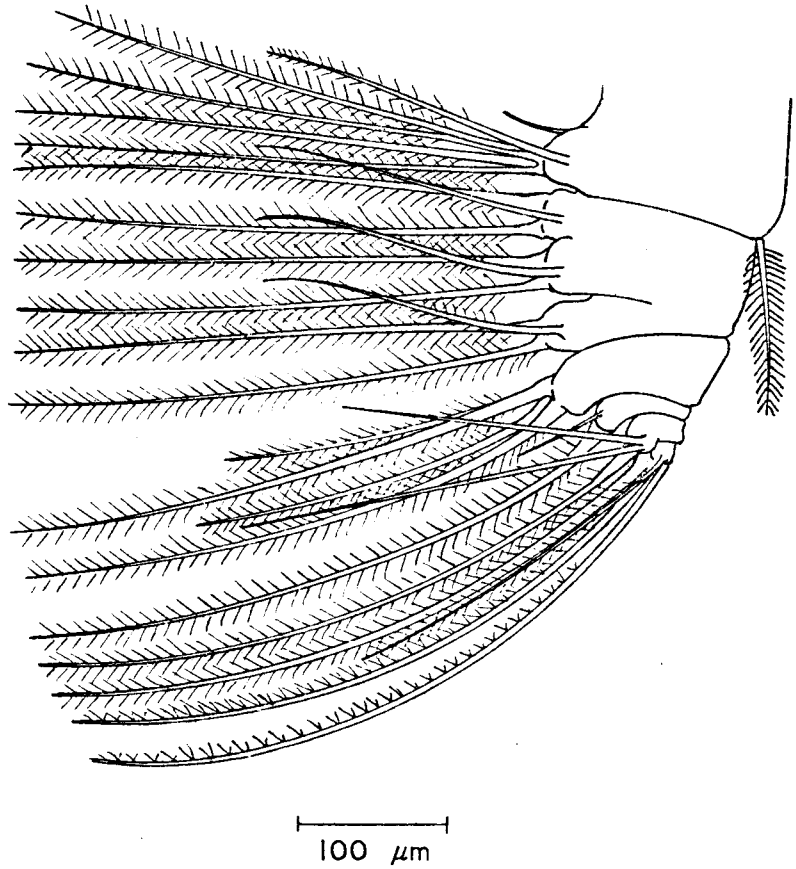
the direction of flux of the spill, and in conveying this organic input both to sediments and to other organisms.

APPENDIX I

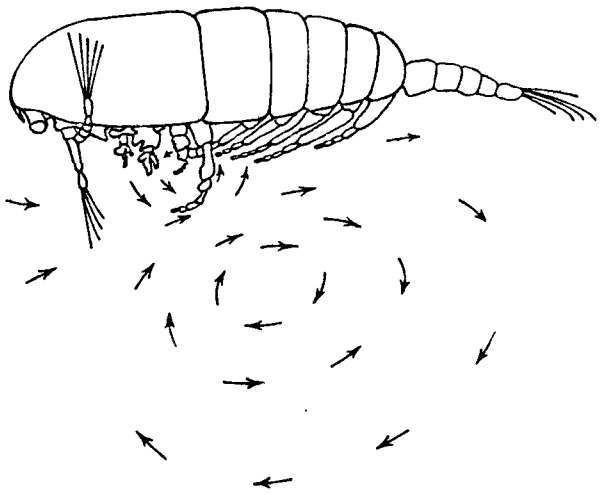
COPEPOD FEEDING MECHANISMS

Feeding Behavior

Herbivorous copepods are filter feeders. Their appendages are modified to form filtering nets with the second maxillae. The maxillae seems to be divided into two portions, a proximal area with smaller mean inter-setullary distance and a distal with greater mean pore size (Conover, 1978). The maxillae are illustrated in Appendix Figure I.1a. The motions of the mouthparts as they beat back and forth in their filtering action will alter the mesh size of the setules, thereby increasing the variances of the intersetule distance (Boyd, 1976); permitting perhaps a wider range of particles to be captured. The second antennae, the mandibular palps, the first maxillae, and the maxillipeds are well developed to produce a pair of feeding swirls. This feeding current is illustrated in Appendix Figure I.1b. The cutting edge of the mandibles is provided with grinding teeth. In predatory species of copepods the mouthparts have few setae and are much simpler. The first and second maxillae, and the maxillipeds are modified as prehensile appendages. The cutting edges of the mandibles have very sharp teeth. The highly serrated margin of a mouthpart allows capture of large particles with an efficiency not estimated from mouthpart area alone (Boyd, 1976). In omnivores, the structures are intermediate, the second maxillae partly used for filtering and partly used much like that of the predators (Anraku and Omori, 1963). The minimum particle size on which the copepods will feed is limited by the minimum spacing of the bristles on the filtering apparatus. In *Calanus*



Appendix Figure I.1a. Feeding appendiges of copepods. The maxilla of *Calanus* (after Gauld, 1966).



Appendix Figure I.1b. Feeding current produced by *Calanus* (after Gauld, 1966).

finmarchicus, for instance, the minimum distance between the finest setules on the female maxillule is 5.7 μm, and the filtration rate is correspondingly much lower for organisms below 10 μm (Marshall and Orr, 1955). In *Pseudocalanus minutus* the spines on the second maxillae are 0.1 mm long, the short bristles are 1-20 μm long, and the average distance between adjacent bristles is 3-5 μm at the distal end. The adults feed most efficiently on cells 5-15 μm in size (Hargrave and Green, 1970).

In experiments, zooplankton generally select the largest food particles in an artificial mixture, but when feeding on a natural population, the animals take mainly the most concentrated particles. Non-perceptive grazers, such as pelagic grazers, will feed over a much greater spectrum of particle sizes than perceptive predators (Conover, 1978). Feeding in *Calanus helgolandicus* is by encounter, but moving prey, such as Artemia nauplii, are sensed from a few millimeters away. Selectivity depended in part on the previous diet (Conover, 1966). Analysis of the pore size may suggest the lower limit for particle size, but it does not explain how the animal can at once feed on particles 25 μm and 75 μm and reject 50 μm particles (Conover, 1978).

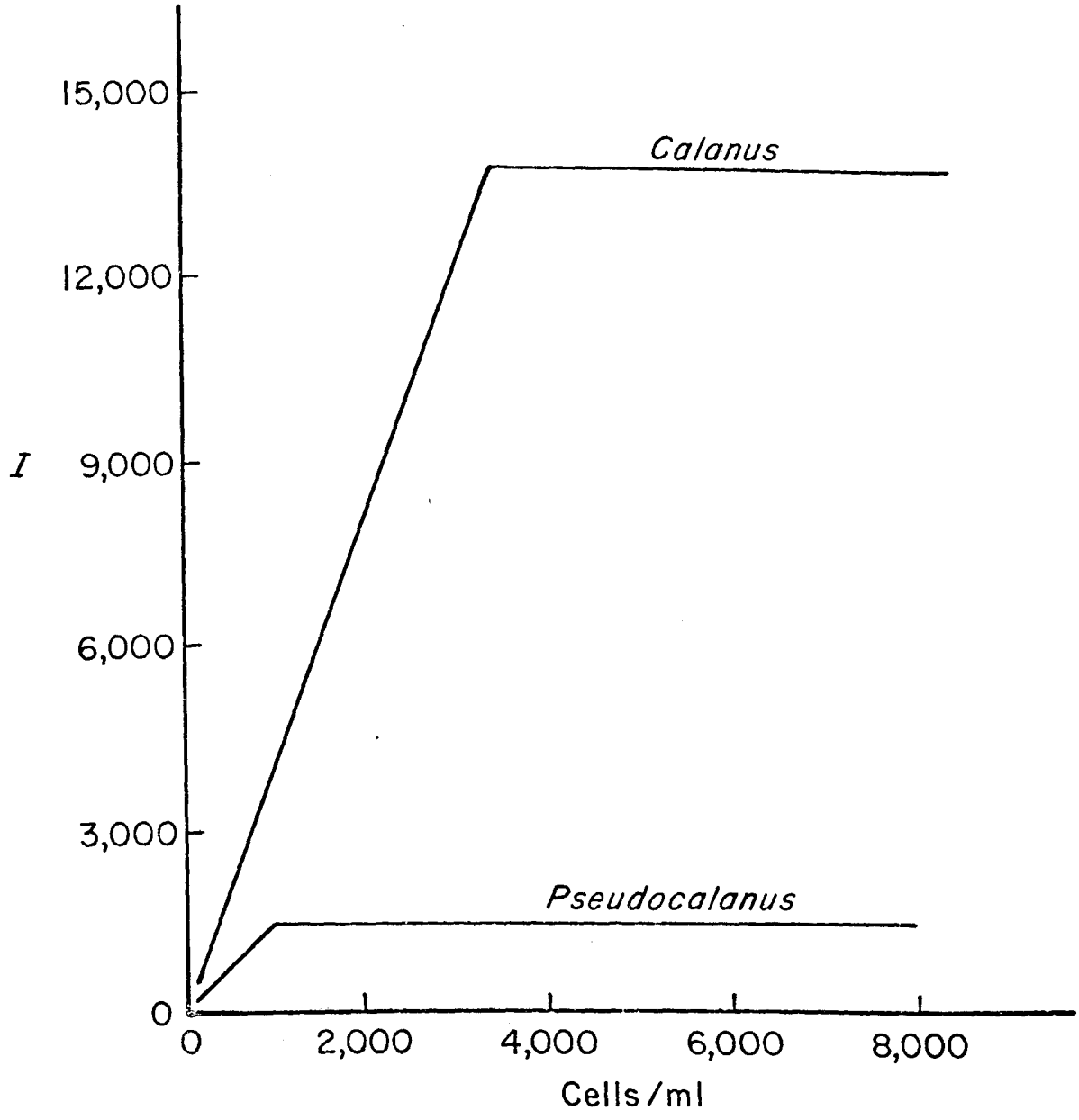
Clearing rate

The grazing rate of copepods is usually given as milliliters cleared per day per copepod. Grazing rates will differ if computed from the total number of cells of all kinds removed or from the total volume of cells removed (Mullin, 1963). Values reported in the literature range from 2-200 ml day^{-1} $copepod^{-1}$. Food density and type, prey density,

and temperature are all factors. Frost (1975) describes the relationship to food density for *Calanus pacificus* as follows: "If food density is such that the animal will obtain less than 15% of its maximum hourly ration while filtering at a maximal rate, then the copepod will feed at a significantly reduced rate. If the copepod may obtain more than 15% of the maximum hourly ration but not all, then the copepod will feed at its maximum rate, and the ingestion rate will be linearly dependent on the density of food. Above the critical food concentration (which also depends on the size of the food particles), the ingestion rate of the copepod is constant". Feeding rates have been shown to decline as prey density increases (Hargrave and Green, 1970), but this may be an artifact of laboratory conditions. The particle size copepods eat varies from 5-350 μm in diameter.

In summary, observations of copepod ingestion patterns may be plotted as two intersecting straight lines, as Appendix Figure I.2 illustrates, suggesting there are different mechanisms limiting ingestion at high and low food concentrations. Below a critical food density the consumption rate may be set by the filtering capacity of the animal. Above that critical density the animals own digestive processes may limit ingestion (Frost, 1974).

Ruminants such as cattle and sheep demonstrate the same graphical pattern when intake is plotted against digestibility of feed. Again, the lower portion of the graph is thought to indicate a physical limitation on intake and the upper graphical region a metabolic limitation (Forbes, 1978).



Appendix Figure I.2. Feeding variations. Adult females of *Calanus pacificus* and *Pseudocalanus* sp. feeding on the diatom *Thalassiosira fluviatilis*. I = cells eaten per copepod per hour (after Frost, 1974).

The existence of superfluous feeding is not conclusively proven, but certain experiments suggest that it may occur (Turner, 1977a). This variability in ingestion and the accompanying variation in assimilation efficiency indicates that treatment of clearing rate or fecal production as constant for a population is a gross simplification. It is difficult to extrapolate from laboratory measurements of the multiple variables which result in these response curves to the natural situation. Appendix Table I.1 reports clearing rate measurements given in the literature.

In order to calculate the amount of food which may be removed from a given volume of water, Appendix Table I.2 cites reported zooplankton densities in Alaskan waters.

Poikilothermic Feeding Strategies

Mathematical models constructed to examine feeding behavior are generally made to examine the behavior of homeotherms, most commonly man himself. However, there are some similarities seen in models for any creature. Output is almost always feeding behavior, expressed quantitatively as amount eaten per unit time. Food intake is discrete, but metabolic machinery operates such that energy is expended continuously. (Although it changes with temperature for poikilotherms.) Due to the complex nature of the physiological mechanisms controlling feeding, both feedback and feed forward mechanisms are necessary if a model is to approach reality. It appears for most animals short-term intake is not related to expenditure, while deprivation is known to stimulate feeding. Animals do not seem to have any way to measure energy per se, cannot

APPENDIX TABLE I.1. Clearing rates.

Copepod species	Food species	Clearance rate	Source
Calanus pacificus	*Thalassiosira fluviatilis*	5.24 ml copepod^{-1} hr^{-1}	Frost, 1975
Calanus helgolandicus	*Lauderia borealis* (1 mg per l)	100 ml day^{-1} animal^{-1}	Gaudy, 1974
Centropages typicus	*Skeletonema costatum*	10 ml day^{-1} animal^{-1}	
Temora stylifera	*Skeletonema costatum*	20 ml day^{-1} animal^{-1}	
Acartia clausia	*Skeletonema costatum*	15 ml day^{-1} animal^{-1}	
Metridia lucens	*Thalassiosira nordenskioldii*	6 ml animal^{-1} day^{-1}	Haq, 1967
Calanus finmarchicus	Diatom sp.	30 to 40 ml animal^{-1} day^{-1}	Marshall & Orr, 1955
Acartia tonsa	*Thalassiosira fluviatilis*	18 ml animal^{-1} (6 hr)$^{-1}$	Anraku & Omori, 1955
Eucalanus pileotus	Mixed organic particles	400 ml copepod^{-1} day^{-1}	Paffenhofer & Knowles, 1979

APPENDIX TABLE I.2.

Location	Density
South Bering surface to 100 m	1500-2500 mg m^{-3} (spring)
Gulf of Alaska surface	20 mg m^{-3} to 150 mg m^{-3}
High polar basin, 100 to 200 m	
Bering and Chukchi Seas	
Arctic Basin 0 to 200 m	0.62 mg dry wt (56 animals) m^{-3}
200 to 900 m	0.14 mg dry wt (13) m^{-3}
greater than 900 m	0.04 mg dry wt (4) m^{-3}
	total biomass above 200 m in central Arctic $1.2 \cdot 10^6$ metric tons dry wt
Arctic Ocean	
South Beaufort	

Alaskan zooplankton densities.

Species	Source
Calanus cristatus, C. tonsus; *Eucalanus bungii*	Zenkevitch, 1963
copepods, 75%; chaetognaths, 15%; miscellaneous, 10%	McAllister, 1961
Calanus glacialis, C. hyperborealis, Metridia longa, Pareuchaeta glacialis	Johnson, 1963
Calanus marshallae, C. hyperboreus, Metridia lucens, Acartia longiremis	Johnson, 1956
copepods	Hopkins, 1969
113 sp. Central Arctic	Grainger, 1965
Acartia longiremis, Calanus hyperboreus, Metridia longa	Grainger, 1975

judge the calories eaten but reach energy balance indirectly through metabolic reactions which are proportional to their energy need (Morgenson and Calaresu, 1978). Mathematically, feeding behavior can be postulated to be controlled by the interaction of two states: one set of local steady states caused by hunger or nutrient deficiency, and the other by satiety. The behavior of this dynamical system is described by a group of differential equations in which the rate of change of each state variable is a function of some subset of the other state variables. The instantaneous state of a dynamical system is thus described by the values of the set of state variables which characterize the system (Barnwell, 1978). It is possible that carnivores, because of their high-energy sources of food, may govern intake more by long-term regulatory mechanisms, while intake of herbivores, whose food is less energy-dense, may be determined more by short-term controls such as full guts and intestinal passage feedback (Panksepp, 1978). Most mathematical models have used one-day cycles for recalculation of variables, thus not dealing with the minute-by-minute changes within the animal which are likely to be closely concerned with meal size, meal interval, and rate of eating (Forbes, 1978).

There are two major differences between poikilotherms and homeotherms which must be considered in mathematical models of their feeding behavior. The first of these is that homeotherms have three major signals for regulation of food ingestion: lipostatic, glucostatic, and thermostatic (Morgenson and Calaresu, 1978). The third of these does not exist for poikilotherms; decreased temperature does not initiate

food intake. The second difference is that, for homeotherms, excluding special situations like growth or pregnancy, energy requirements are constant across the seasons and the basal metabolic rate does not change (Hirsh, 1978). The basal metabolic rate of poikilotherms drops as the temperature drops and thus their energy requirements are less (Vernberg and Vernberg, 1970). A third difference for the particular poikilotherms studied in this paper is caused by the patchiness and seasonal changes in the animals food supply. Since food is plentiful only at one time of year, food intake must be regulated not only by the animals internal environment but by opportunistic considerations of maximum ingestion while the food is available. Thus, the animals energy balance changes across the year as the animals store energy during spring bloom and summer and deplete their reserves while overwintering.

Interaction with Oil

While experimental observations, as mentioned in Chapter 2, have shown that oil may be ingested, it is not possible to determine whether it was adhering to the surface of food particles, or whether it was ingested as an intact oil droplet the organism could not or did not choose to avoid in its grazing process. The facts that copepods are able to select for particles and for particle size, and will not graze on undesirable particles, and that food is sometimes rejected after it is brought to the mouth, suggests that a chemoreceptive sense does exist (Conover, 1966). However, copepods have ingested plastic beads in feeding experiments (Wilson, 1973). Not much is known about the mechanisms or criteria

of this sense, or whether an oil droplet meets the criteria. It appears possible that in the filtering process an oil droplet may simply impact on the filtering bristles and adhere so that it must be ingested.

This uncertainty in the actual process and reason for oil ingestion makes prediction of ingested oil from a known concentration of oil droplets in the water questionable. The amount of phytoplankton contaminated with oil or the quantity of this oil is generally difficult to establish, but this may be the major mode of entry into zooplankters. The possibility of uptake of soluble fractions of oil through drinking water or phytoplankton uptake is another unknown. Observations of the copepods *Calanus* sp., *Temora stilifera, Diaptomus* sp., *Heterocope salieris*, and *Cyclops strenuus* did not demonstrate any oral water-swallowing (Fox, 1952).

Comparison of oil droplets to phytoplankton

From Forrester's observations of the *Arrow* oil spill (1971) we may obtain an idea of the physical characteristics of oil droplets compared to those of phytoplankters. Appendix Table I.3 gives the mean values for particles between 5 and 85 μm found by Forrester. Appendix Table I.4 cites characteristics for common phytoplankters in order to compare these oil droplets with normal food particles. It may be seen that the oil droplets fall within the ranges cited for both phytoplankton cell volume and weight. Appendix Table I.5 cites phytoplankton densities observed in Alaskan waters. These densities may be compared to the oil droplet densities found by Forrester. An oil concentration of 1 ppm of droplets less than 100 μm in diameter, assuming each particle weighs 0.2 μg, would be a droplet concentration of $5 \cdot 10^6$ particles m^{-3}.

APPENDIX TABLE I.3. Oil droplet observations

(Calculated from Table 1; Forrester, 1971).

volume per particle	$1.39 \cdot 10^{-9}$ to $0.6 \cdot 10^{-6}$ cm^3
average volume per particle	$0.2 \cdot 10^{-6}$ cm^3 = $0.2 \cdot 10^{6}$ μm^3
particles per liter	18.1
average mass per liter	3.6 $\mu g \cdot \ell^{-1}$ = $3.6 \cdot 10^{-3}$ g m^{-3}
average mass per particle	0.2 μg

APPENDIX TABLE I.4. Phytoplankton characteristics.

Species	Vol. (μ^3)	Dimensions	[C]	Source
Ditylum brightwelli	$1.2 \cdot 10^5$	100 µm·50 µm	$1.9 \cdot 10^{-8}$ pg C cell^{-1}	Mullin, 1963
Rhizolenia setigera	$7.6 \cdot 10^4$			Mullin and Brooks, 1967
Gymnodinum nelsoni	$7.5 \cdot 10^4$			Mullin and Brooks, 1967
Striatella unipunctata	$6.9 \cdot 10^4$			Raymont and Gross, 1942
Gonyaulax polyedra	$3.0 \cdot 10^4$			Raymont and Gross, 1942
Thalassiosira fluviatilis	$2.3 \cdot 10^4$		$1.4 \cdot 10^{-4}$ µg C cell^{-1}	Conover, 1966
Cyclotella nana	$2.1 \cdot 10^2$		0.041 µg C cell^{-1}	
Coscinodiscus conginnus	$6.9 \cdot 10^6$	330-335 µm, 100-150 µm	0.06 µg C cell^{-1}	
Coscinodiscus wailesii	$1.6 \cdot 10^7$		$1.5 \cdot 10^2$ µg C cell^{-1}	
Lauderia borealis		40-48 µm		Corkett and Urry, 1968
Isochrysis galbana		4-8 µm		Corkett and Urry, 1968
Nitzschia closterium		3-4 µm, 25-35 µm		Gauld, 1951

APPENDIX TABLE I.5. Phytoplankton productivity.

Area	Cell Density	Production	Remarks	Source
S. Gulf of Alaska		0.01 g wet m^{-3}	>150 m May	Damkaer, 1976
S. Bering Sea	$1.71\text{-}4.68 \cdot 10^{6}$ cells ℓ^{-1}	$2.4\text{-}6.6 \cdot 10^{-4}$ g C ℓ^{-1}		Alexander, 1976
N.E. Gulf of Alaska		.4 g C m^{-2} day^{-1}		Larrance, 1976
Prince William Sound	2000 cells ℓ^{-1}	$.28 \cdot 10^{-6}$ g C m^{-3}		

Conover (1971) studied the copepod population in the area of this oil spill. He suggests the following method for estimating grazing by the animals upon oil droplets. Knowing the standing crop of zooplankters, assuming 10% of the wet weight is organic matter, and food equal to 15% of the animals organic matter is grazed daily, one may calculate the amount grazed. Multiplying the amount grazed by the percentage of oil weight to natural organics gives the amount of oil ingested.

This thesis has resulted in a different approach for calculating estimations of oil grazing by copepods, not necessarily a better or simpler method. This thesis has attempted to understand how it comes about that a copepod will ingest an oil droplet. It is postulated that the characteristics of the ambient phytoplankton have a great deal to do with the animals choice of maintaining feeding behavior in the presence of oil droplets. The validity of this approach can only be answered by further experimental work.

APPENDIX II

HYDROCARBONS

Introduction

Petroleum is derived from the organic compounds of past organisms under conditions of long-sustained high heat and pressure. These conditions alter petroleum hydrocarbons somewhat from their biogenic sources, but some of the relationships may still be traced.

While the bulk of fossil petroleum contained in deposits in the earth was not formed directly from hydrocarbons, but rather through transformation of organic compounds in once-living tissues, plants and animals do synthesize hydrocarbons directly. They are not present in large amounts but are universal, present in all plants and animals, and released into their surroundings. Hydrocarbons are not readily metabolized and so have been disregarded as a dead end of metabolic processes. However, recent work with algal tissues suggests straight-chain hydrocarbons may be more important in cell biochemistry and cell growth than previously contemplated (Youngblood and Blumer, 1973). Hydrocarbons result from highly endergonic metabolic processes and possess the highest potential energy of any class of biochemicals. Their occurrence in organisms is generally in association with the lipid fraction. Studies of zooplankton from tropical versus arctic waters have demonstrated the importance of lipid, and the class of lipid, in controlling buoyancy and as reserve energy supplies for the zooplankter (Lee and Hirota, 1973).

When a hydrocarbon is produced by an organism, it tends to persist and to be passed relatively unchanged within the food web, and in transfer to the water column and the sediment. Some organisms have even evolved specific mechanisms for the retention of certain hydrocarbons from their food (Blumer *et al.*, 1970).

This stability of hydrocarbons, coupled with their variety, makes them a potentially valuable tool as labels in tracing marine food webs, the migration of marine species and movement of water masses (Blumer *et al.*, 1963).

The dependency of man's economic system on fossil hydrocarbons; and the importance of biogenic hydrocarbons, and of their value as tracers of food web connections, have made hydrocarbons an object of study in the past. During the past decade a new reason has evolved for that study. With rapidly growing expansion in oil extraction and transportation, the ocean is beginning to receive a large input of fossil hydrocarbons through accidental spills, etc. At present the ocean receives approximately an equal contribution from living organisms and from pollution (National Academy of Sciences, 1975). The question of what happens to those pollutant hydrocarbons has become worrisome. They have been shown in experiments to be toxic and to have been concentrated and transferred in the food web (Barnett, 1973; Corner *et al.*, 1976). It is sometimes difficult to distinguish natural from pollutant hydrocarbons. It is not necessary for all organisms to concentrate or transfer hydrocarbons for petroleum pollutants to be dangerous. Magnification of the concentration of toxic compounds in

organisms up a food web will occur and may be dangerous even if the pollutant is concentrated only by a very few species (Blumer *et al.*, 1970). Species such as the calanoid copepods discussed in this paper make up approximately 80% of the plankton biomass in some areas (McAllister, 1961).

Biogenic Hydrocarbons and Lipids

Hydrocarbons occur in all marine organisms but generally account for 1% or less of the total lipid. Naturally occurring marine hydrocarbons may be regarded as four distinct groups: a) a series of normal saturated or monounsaturated long chain hydrocarbons, b) polyunsaturated normal hydrocarbons, c) monomethylbranched hydrocarbons, and d) terpenes (e.g., squalene and pristane). Marine bacteria generally produce monomethylbranched hydrocarbons while most marine algae are rich in polyunsaturated normal hydrocarbons. The lipids of most marine organisms contain a hydrocarbon series ranging in chain length from C_{13} to C_{33} with an odd chain predominance (Youngblood and Blumer, 1973). The principal lipid classes usually detected in zooplankton are phospholipid, triglyceride, hydrocarbons, steroids, diglycerides, and wax esters (Morris, 1971).

A basic simplicity to the hydrocarbon composition of clean marine organisms is apparent. Only a small number of compounds is present, some apparently biochemically-favored structures dominate considerably, most compounds are olefinic, and there are few branched and cyclic compounds and no aromatic hydrocarbons in the C_{13}-C_{24} range (Youngblood

and Blumer, 1973). This is quite different from the complex spectra of petroleum hydrocarbons. Petroleum is a mixture containing greater ranges in molecular weight and structure than biogenic hydrocarbons. Petroleum contains several homologous series, where the adjacent members are usually present in nearly the same concentration. More kinds of cycloalkanes and aromatic hydrocarbons are present (National Academy of Sciences, 1975). Appendix Table II.1 shows characteristic lipid levels in polar plankton.

The majority of biochemical analyses published deal not just with hydrocarbons, but with total lipid or fatty acid analysis. However, hydrocarbons with an unbranched carbon skeleton have an evident biogenic relation to fatty acids. The predominance of odd-numbered compounds in an organism's hydrocarbon spectrum is a biogenic indicator for their origin from even-numbered fatty acids. The fatty acid spectra of marine lipids is complex, and its composition in a particular organism appears to be characteristic for that species of plant or animal (Scheuer, 1973).

There is little experimental evidence for marine algae, but it is quite likely that decarboxylation of a fatty acid to a hydrocarbon is the major pathway for hydrocarbon synthesis. This mechanism only explains the formation of odd chain hydrocarbons with chain lengths less than the naturally occurring fatty acids. The biosynthetic pathway for the formation of hydrocarbons of chain lengths greater than C_{26} has yet to be found (Sargent *et al.*, 1976). It is necessary to understand the pathways for biogenic synthesis of lipid compounds in order to evaluate the potential areas of impact of petroleum compounds, and which trophic

APPENDIX TABLE II.1. Lipid levels in polar plankton (Lee and Hirota, 1973).

Plankton Group	Triglycerides	Wax esters	% Lipid of dry weight	mg Lipid per individual
Calanus finmarchicus	11%	63%	50%	0.22
Calanus hyperboreus	27%	92%	73%	5.9
Euchaeta sp.	4%	61%	31%	0.16
Metridia sp.			34%	0.06
Chaetognaths		25%		0.8
Mollusca		<57%		0.4-14.0
Euphausiacia		<57%		144-2.8
Decapod		32%		1.2-32.9
Mysidicea				12.5
Amphipoda				0.14

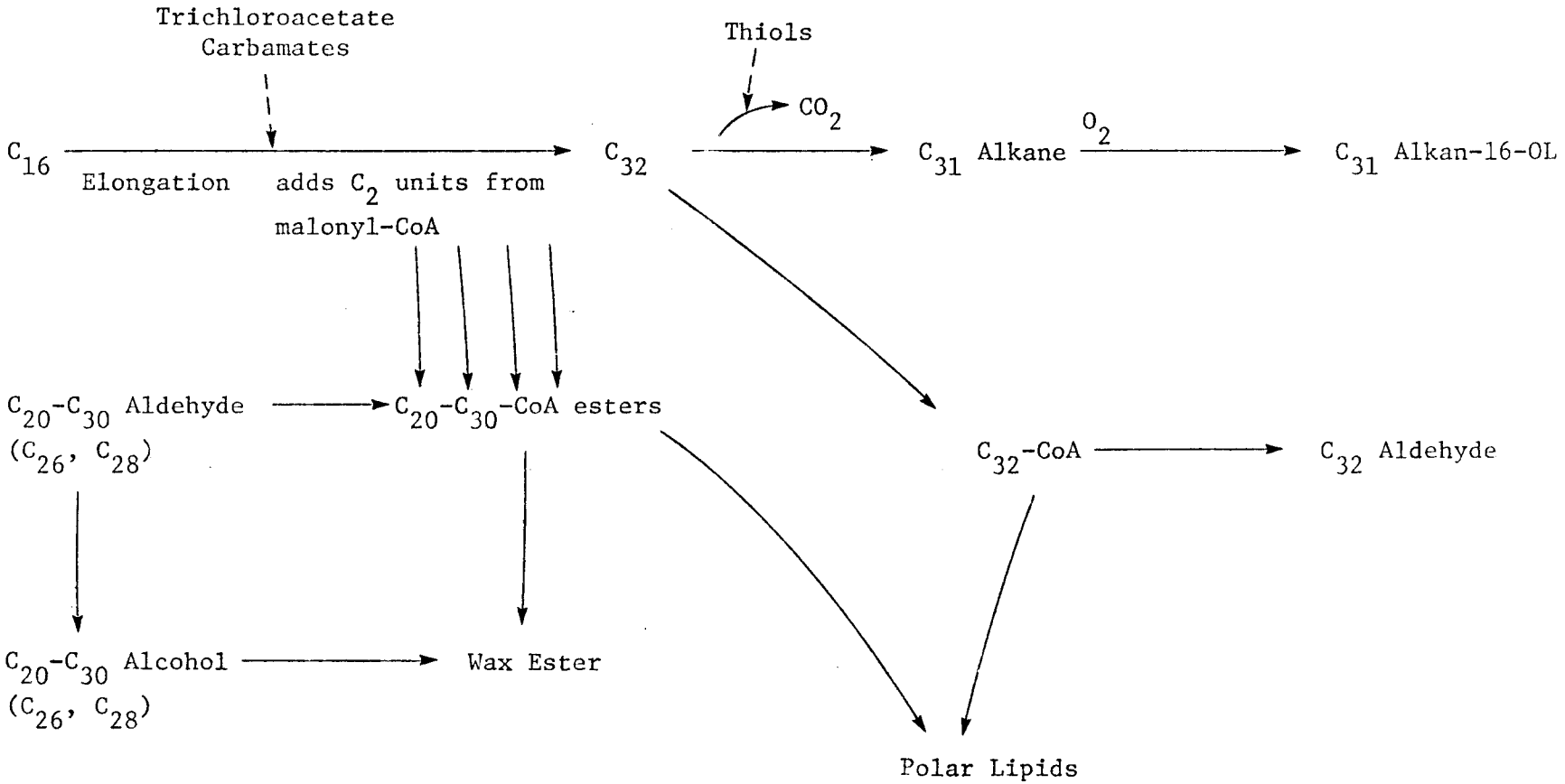
Plankton groups are from upper 500 m.

levels are most important or most vulnerable. Appendix Figure II.1 presents proposed pathways for the synthesis of the various lipid classes.

Biogenic food webs

Pristane (2,6,10,14-tetramethyl-pentadecane) is a hydrocarbon which occurs in unusually high concentrations in copepods of the genus *Calanus*. It has been found in concentrations of up to 0.5% in various crude oils (Blumer *et al.*, 1963) and is found in various geological sediments. The presence of pristane in these geological formations has been considered evidence for a biological contribution to the formation of hydrocarbons in nature. The liver of the basking shark has also been shown to contain pristane in levels correlated with the ingestion of *Calanus* sp., relative to other food sources (Blumer, 1967).

Pristane is one of the most studied biogenic hydrocarbons. It is widespread and often the only hydrocarbon found in analysis of copepod lipids. It is refractory, passes unchanged to higher trophic levels, and so has often been proposed as a tracer for food webs or for water masses when contained in a dissolved state. Three isomeric C_{19} monoolefins with the carbon skeleton of pristane have been detected in mixed zooplankton and from the liver oils of some marine fishes and animals. The isomers are: 2,6,14 trimethyl-10-methylene pentadecane: 2,6,10,14-tetramethyl-1-pentadecane (norphytene or zamene); and 2,6,10,14-tetra-methyl-2-pentadecane (Blumer and Thomas, 1965). The precursor of pristane is thought to be phytol, which occurs as an ester in chlorophyll. Phytol would be oxidized to phytanic acid (a fatty acid), then



APPENDIX Figure II.1. Hypothesis for lipid biosynthesis pathways (from Kolatlakudy, 1975).

decarboxylation would take place to produce pristane (Avigan and Blumer, 1968).

Other copepods such as *Metridia lucens, Rhincalanus nasutus, Euchirella rostrata, Pleuromamma robusta, Paraeuchaeta novegica, Nematoscelis magalops*, and *Maganyctiphanes norvegica* contain, relative to their dry weight, much less pristane (or none) than *Calanus* sp. The fact that pristane originates in such a specific source, plus its metabolic refractoriness, make it so attractive as a tracer.

Another hydrocarbon which appears to be an attractive tracer compound is HEH (all-cis-3, 6, 9, 12, 15, 18-heneicosohexaene). It is an olefin found in many planktonic algal species, probably a metabolite of the common $C_{22:6}$ ($\Delta 3$) fatty acid (all-cis-4, 7, 10, 13, 16, 19-docosahexaenoic acid) *via* decarboxylation. HEH can compose over 1% of the dry weight of some diatoms (Bacillariophyta) and Chryosophyta. The copepod *Rhincalanus nasutus* accumulates HEH non-selectively from its algal food together with the triglyceride lipids. Other related copepods do not accumulate HEH even when it is available (Blumer *et al.*, 1970).

These compounds are important because they illustrate the stability and persistence of hydrocarbons within the food web. Their existence indicates a possibility that a petroleum compound may follow this sort of magnification pathway. Those organisms without enzyme systems capable of metabolizing the compound may find it toxic.

Food chains which begin with algae, go through zooplankters and ending in higher trophic levels, such as fish, sharks, or birds; seem to derive their basic lipid patterns from algal sources. The fatty acids in

the fauna are largely unchanged from the algal fatty acids (Jezyk and Penicnak, 1973). Copepods appear to incorporate them directly into their energy reserves (wax esters) (Lee *et al.*, 1971). Pristane and HEH, as has been mentioned, become concentrated in higher trophic levels without change.

From the foregoing, it appears that transportation and concentration of biogenic hydrocarbons does occur in the food web. Because the basic pattern of lipid composition is set by phyto- and zooplankters, nekton organisms which could themselves avoid polluted water cannot avoid pollution assimilated by their prey. The influence of ambient conditions on lipid composition would doubtless be reflected in the effect of pollutant hydrocarbons. Polar organisms, with their unique composition emphasizing stable storage lipids and one dominant hydrocarbon, will be affected differently than tropical organisms. Zooplankters such as polychaetes, ctenophores, chaetognaths, and mysiids also have little storage lipid and might be expected to show different reactions to pollutants (Lee and Hirota, 1973). Lipids thus are a significant portion of the biomass being transferred in food webs. Their quality will seriously affect the quality of the entire food web and those higher trophic levels in which man has commercial interest, since lipids are the biogenic energy reserve.

Hydrocarbons in the water column

As phytoplankton and zooplankton, or members of higher trophic levels, die or decompose, some of their lipid materials and hydrocarbons

are released into the water column in a dissolved state. As mentioned previously, these materials may provide tracers for water masses. It is also possible that other organisms reabsorb these hydrocarbons, or that the hydrocarbons form colloidal particles which may be ingested. Petroleum hydrocarbons are also found along with those of biogenic sources. At certain times of the year dissolved hydrocarbon levels are quite high due to biogenic terrestrial input, and may even outweigh low level pollutant influxes; as has been suggested for Port Valdez (Button, personal communication). Thus, when attempts are made to assay the importance of pollutant hydrocarbon influxes, it is wise to ascertain the biogenic ambient hydrocarbon level in the water column. Appendix Table II.2 lists some measurements cited in the literature for ambient hydrocarbon levels in various areas of the world.

Petroleum

Petroleum characteristics

The types of petroleum products which most frequently impact the marine environment are crude oils, Bunker C or No. 6 fuel oils, diesel or No. 2 fuel oils, and light petroleum products such as kerosenes or gasolines. There are thousands of individual compounds in petroleum. Varying proportions of each characterize oils from different regions or refinement degrees, and determine the physical and chemical properties which influence their effect in the marine environment (National Academy of Sciences, 1975). Appendix Table II.3 details some of the characteristics of petroleum and its distillate fractions.

APPENDIX TABLE II.2. Oil in seawater.

Area	Surface	Particulate		Dissolved		Source
		Near-surface	Near-bottom	Near-surface	Near-bottom	
	µg ℓ^{-1}	µg ℓ^{-1}		µg ℓ^{-1}		
Gulf of Alaska				0 - 9.53		Shaw, 1977
Cook Inlet				0.18- 1.12		
Norton Sound & Chukchi Sea				0.13- 1.41		
Beaufort Sea				0.24-27.59		
World values	0-1200			0.11- 5.66		Marty & Saliot, 1976
Georges Bank						
winter	54	0.28±0.29	0.46±0.73	29.6±15.3	35.3±24.8	Boehm *et al.*, 1979
spring	20	0.39±0.52	0.23±0.14	12.3±12.7	10.0± 9.8	
summer	11	0.35±0.53	0.09±0.08	1.0± 1.0	1.9± 2.7	
fall	?	0.06±0.10	0.04±0.04	0.2± 0.2	0.8± 1.5	
Bedford Basin				1-50		Keizer & Gordon 1973

APPENDIX TABLE II.3. Characteristics of a typical crude oil (National Academy of Sciences, 1975).

By molecular size:

gasoline (C_5 - C_{10})	30%
kerosene (C_{10} - C_{12})	10%
light distillate (C_{12} - C_{20})	15%
heavy distillate (C_{20} - C_{40})	25%
residuum oil (> C_{40})	20%

By molecular type:

paraffin hydrocarbons	alkanes	30%
naphthene hydrocarbons	cyclo-alkanes	50%
aromatic hydrocarbons		15%
nitrogen, sulfur, oxygen-containing		5%

NB: crudes from different sources can vary considerably from the above averages.

Physical characteristics of distillates:

	Specific gravity	Viscosity	Pour Point	Distillate
Bunker C or #6 fuel oils	1.00	1,000 centipoise	21°C	heaviest
Diesel or #2 fuel oils	0.825-0.850	40	-20.5°C	middle
kerosene	0.500	1-2		light
gasoline	0.700	<1		light

APPENDIX TABLE II.3. Continued.

Chemical composition of distillates:

	Naphthenes	Paraffins	Aromatics	NSO	C-# Range
Bunker C or #6 fuel oils	45%	15%	25%	15%	$>C_{30}$
Diesel or #2 fuel oils	45%	25%	30%		C_{12}-C_{25}
kerosene	50%	35%	15%		C_{10}-C_{12}
gasoline	40%	50%	10%		C_5 -C_{10}

Middle and light distillate fractions are mixtures of virgin petroleum and catalytically or thermally cracked components. Blended gasolines have a higher aromatic content (20-30%).

There are various estimates for the amounts of petroleum impacting the ocean. The National Academy of Science (1975) estimates the inputs for the early 1980s as follows. River runoff is the main source of pollutant hydrocarbons entering the ocean [1.6 metric tons per annum (mta)]. Of course, this is felt most strongly in coastal areas. Transportation processes are the second biggest source (0.8 mta), followed closely by atmospheric input (0.6 mta), natural seeps (0.6 mta), and municipal and industrial wastes (0.45 mta), and then offshore production (0.2 mta). It is interesting that the total entering the ocean, 4.57 mta, is less by a factor of 10 than the amount entering the atmosphere. However, most of the petroleum hydrocarbons entering the atmosphere undergo reactions there and do not return to the earth's surface in that form. Most petroleum fractions have a much higher solubility in lipid materials than in water. Therefore, most organisms tend to absorb oil hydrocarbons upon exposure. Knowledge of the metabolism and function of biogenic hydrocarbons will aid in prediction of the fate and effects of petroleum hydrocarbons which have entered the planktonic environment.

The complex composition of petroleum implies a possibly wide range of impacts upon an organism and its physiological functioning; effects upon: lipid metabolism, membrane permeability and function (e.g., osmoregulation), salinity and temperature tolerance, metabolic rate, sensory physiology (interference with chemoreception, for instance, would bias food selection, homing, or any behavior related to pheromones), reproductive success, and behavior (IDOE, 1971). Petroleum has been shown to cause a loss of the protective membrane coating on the gills, changes in

liver fat and fatty acid composition, and to preferentially invade nerve tissue (National Academy of Sciences, 1975).

Oil in the food web

Oil may enter into the food web in several ways. It may adhere to the surface of particles, both living and dead, which are later ingested. Actual oil droplets may be eaten. *Via* this route, pelagic organisms, which otherwise have the mobility to avoid an oil plume, may become contaminated. Active uptake of dissolved or dispersed hydrocarbons also occurs, mainly through the gills, or by filter feeders searching for food. Passage into the gut with drinking water is also possible. It is expected that pollutant hydrocarbons would be absorbed through the guts of animals along with lipids from the food. The ability to select and discriminate in hydrocarbon uptake has often been demonstrated (Teal, 1977; Blumer *et al.*, 1970). Accumulation of hydrocarbons is a process of lipid-water partitioning. Blood from gills passes through muscles before reaching the digestive system and liver; thus hydrocarbons absorbed from water tend to be localized in the muscle. It appears that uptake in the gut is more efficient for hydrocarbons in the C-20 to C-30 range (Teal, 1977).

Often the response of an organism to a pollutant exposure is to accumulate the pollutant fairly rapidly at first and then to reach a plateau. What happens to the pollutant after uptake is a function of the organism's ability to metabolize and/or excrete the pollutant or its metabolites. Depuration is often a reverse of the uptake, with an initial rapid loss rate, decreasing slowly to a plateau containing long-term

residues. A return to precontamination levels is usually not found. The form in which a compound moves through the food web will be vital in the effect it has. The metabolites of aromatics are more toxic and more water soluble than the parent compound (Teal, 1977).

Marine organisms differ significantly in their ability to degrade hydrocarbons. The liver, or the liver-like organ of invertebrates, the hepatopancreas, is thought to be the site of hydrocarbon degradation. In these organs hydroxylation and other reactions are completed to detoxify the hydrocarbons. Marine fish and some marine invertebrates have been shown to be able to degrade aromatic and paraffinic hydrocarbons. In experiments with various copepod species, several were unable to metabolize aromatic hydrocarbons, but could degrade paraffinic hydrocarbons. In other experiments, phytoplankton, some benthic marine invertebrates and some zooplankton species were unable to oxidize either paraffinic or aromatic hydrocarbons (National Academy of Sciences, 1975). Zooplankton seem to be the variable group of organisms. In a study of zooplankton species from the arctic, British Columbia, and California; copepods, euphausiids, amphipods, crab zoea, ctenophores, and jellyfish rapidly took up labeled aromatic hydrocarbons. The crustaceans were able to metabolize these to hydroxylated and more polar metabolites, but the ctenophores and jellyfish were unable to metabolize the aromatics. Little storage of metabolites was detectable. Depuration ranged from 17-28 days with a small residue remaining after that. Active feeding during depuration enhanced the depuration rate. Concentrations of 200-500 ppb produced sublethal effects; 500 ppb was lethal for some animals after

24 hours. The hydrocarbons were metabolized and discharged faster when they were absorbed to ingested algae (Lee, 1975). A direct lethal response has been found in most adult marine species from exposures of 1-100 ppm (parts per million) SAD for several hours exposure (SAD is an abbreviation for soluble aromatic derivative hydrocarbons). For pelagic crustaceans the range is 1-10 ppm, and for larvae 0.1-1.0 ppm. The latter concentration range has also been shown to produce sub-lethal effects in adult organisms (Moore and Dwyer, 1974).

The dietary route of entry is more important quantitatively than direct uptake from solution. In experiments in which *Calanus helgolandicus* was exposed to naphthalene, depuration was rapid after accumulation from the salt water solution. When accumulation was *via* the diet, depuration was appreciably slower. Metabolism of the naphthalene did occur to some extent (Corner *et al.*, 1976). Uptake has a linear relationship with the concentration in water. The best correlation occurs between lipid content and uptake when accumulation is directly from solution; for the dietary route there is no correlation. Exposed larvae retain 5-30% of the accumulated pollutant to the adult stage (Corner *et al.*, 1976).

The difficulty in predicting the consequences of an oil leakage lies in the fact that lethal effects may be diminished or vastly maximized by the interaction of environmental conditions with the location and timing of the pollutant release. Oil may act upon biota indirectly through alteration of the habitat. Nekton or intertidal organisms directly in the path of an oil plume may become externally coated with an oil layer, resulting in respiratory or osmotic difficulties, or possibly

in oil ingestion as the organism attempts to clean itself. Oil ingested by organisms may be incorporated or passed on in the food web. All of these oiling impacts may result in lethal or sublethal effects which may become widely spread through the ecosystem. Sublethal effects, of course, are much more difficult to observe or measure but ultimately they may have consequences which are far more detrimental to the survival of the population as a whole. The type of oil and the amount of mixing it undergoes are also of critical importance. One of the causes for the wide variability in experimental data obtained from oil toxicity tests is that many experiments were conducted without adequate delineation of these parameters.

The aromatic fraction of oil is the most toxic component, perhaps because there is no biogenic counterpart. Metabolic breakdown is generally quite slow. Work by Malins (1977) suggests that many environmental chemicals such as chlorinated hydrocarbons or various metals, may influence the enzyme system responsible for the metabolism of aromatic hydrocarbons. Low temperatures may also inhibit these enzymes. Thus, synergistic conditions will force increased pressures upon organisms. The toxicity of naphthalene and benzene has been found to be directly related to the degree of alkyl substitution (Caldwell *et al.*, 1977), as the organisms lack the enzymatic machinery to degrade these structures. Some polycyclic aromatic hydrocarbons are carcinogenic. The presence of low to medium boiling point aromatic hydrocarbons in concentrations as low as 10-100 ppb may be inhibitory to most marine species. Whether or not higher boiling insolubles affect a species depends on the degree to which

the specific physical nature of the substrate is altered by oil, and how that change affects the utilization of the substrate (Moore and Dwyer, 1974). Fortunately, aromatic hydrocarbons are also the most volatile components of oil, thus the major portion of aromatics are removed to the atmosphere in the first 48 hours after release. Once the oil has been sedimented, however, there is not much further loss of toxic hydrocarbons. Many oil-water separators or similar treatments are not effective in reducing aromatics, even though figures for total removal make the treatment appear effective.

Oil trajectories

What happens to petroleum once it enters the marine environment depends upon the circulation patterns and climatic conditions at the point of introduction, but is influenced most by the physical and chemical nature of the oil. As a spill ages from time of entry, the importance of the different dispersive and degradative processes changes from rapid physical effects to slower chemical and biological modifications. In the first stages the spill spreads quickly into a thin layer. Gravity, viscosity, the influence of the surface-active constituents (containing nitrogen, oxygen, and sulfur) are important here. Wind, waves, and current also play a part in determining slick growth.

Past meteorological data is used to aid in prediction of oil spill trajectories. Prevailing winds and storm patterns may be identified with the time of year but there is still too much variability to make exact predictions possible. Appendix Table II.4 lists meteorological and

APPENDIX TABLE II.4. Alaska physical description.

Location	Current patterns & speed	Storm & wind patterns	Source
E. Cape St. Elias	westward flow		Galt & Pease, 1977
W. Cape St. Elias	2 gyres: near shore weak counter-clockwide gyre carries offshore water in toward coastline south of Copper River; offshore stronger clockwise gyre carries water offshore past Cape St. Elias		
Port Valdez	no constant pattern; inflow and outflow average 2-3 cm sec^{-1}, narrows 20 cm sec^{-1}	max winds Jan-Feb easterlies common during winter	Hood *et al.*, eds., 1973
Aleutian-Commander Is. Arc-Bering Sea	flow variable in direction and magnitude; surface strait currents 5-18 cm sec^{-1}; mean northward flow 14 sverdrups		Favorite, 1972
Norton Sound	current direction alternates with diurnal tidal frequency from east to west; cyclonic circulation north of St. Lawrence Is. brings very cold water to west edge of sound; summer water characteristics influenced by river input, wind transport and mixing; winter water characteristics controlled by thermohaline convection	frequent and sometimes severe summer storms	Hood *et al.*, 1974

APPENDIX TABLE II.4. Continued.

Location	Current patterns & speed	Storm & wind patterns	Source
North Alaskan Coast		Easterly winds predominant, then westerly (others total 30%); primary storm track from Siberia; average 2 storms per month in winter	Hufford, Lissauer, Thompson, 1977

current patterns for some Alaskan areas with possible effects upon oil trajectories. Appendix Table II.5 cites some oil trajectory models with their conclusions. In the discussion of phase 4 in this thesis, these trajectory models are simply used to suggest possible directions for movement of the contaminated water mass.

The surface-to-volume ratio is increased greatly by the spread of oil, and so evaporation becomes the key dispersal mechanism (National Academy of Sciences, 1975). Evaporation may remove about 50% of the hydrocarbons in an average crude oil in a surface slick. After the loss of the more volatile compounds, the oil is less reactive. Photochemical and biological degradation become dominant. Soluble compounds, the lower molecular weight hydrocarbons, and the more polar nonhydrocarbon compounds, dissolve into the water column. Biological and chemical oxidation processes will produce more polar compounds (alcohols, fatty acids) from oil hydrocarbons. As these processes continue, the remaining oil becomes more and more dense, viscous, and refractory. Tarry residues form, and interaction with the environment is slow. Microbial degradation becomes the active process (National Academy of Sciences, 1975). Once oil has become sedimented, estimates of its residence time vary from 3-10 years, depending on the sediment particle size, nutrients, light, temperature, current exposure, and microbial fauna (Moore and Dwyer, 1974).

In the arctic, there are two factors which will drastically affect the nature of an oil spill. The factors are: 1) the existence of pack ice, and 2) low ambient temperatures. Low temperatures would inhibit

APPENDIX TABLE II.5. Oil trajectory models: theoretical and experimental.

Source	Assumptions	Predictions
Okubo, 1970	Presence of velocity singularity=convergence of foreign particles initially arranged in a circle surrounding the singularity	Circle will be deformed into ellipse
Weiskopf & Uzuner, 1977	Used crude oil and #2 fuel, ice cover and current	Spreading phases involve gravity, inertia, viscous and surface tension forces. Additional spreading phase occurs in presence of current. Phase controlled by balance between drag of water on iced slick and retarding force of ice sheet on oil slick.
Hess & Kerr, 1979	Spill vol. 1.3×10^6 gal, calm water	Radius of spill (mi): 1.5×10^2 (1 hr), 10^3 (1 da), 1.5×10^3 (1 wk), 10^4 (1 mth)

all of the degradative processes previously mentioned as well as changing the physical properties of oil such as viscosity. For this reason, biologists have theorized that oil spilled into the arctic would remain for 50 years (Campbell and Martin, 1973). Lack of light in winter months would prevent photochemical oxidation. Viscosity would be increased by the low temperatures, making the oil less susceptible to weathering processes. Evaporation and solubility would be decreased by cold temperatures. As the oil spills onto pack ice, it would disperse through open leads and over the ice surface with the movement of melt water caused by albedo changes. Oil emulsions would form in the leads and be driven under the ice by wind shear or local ice convergence. As floes at the surface are driven by storms, they would move faster than the oiled layer below, so a large area of ice would be driven over the oil. The action of ridges moving through the oil would act to disperse the oil laterally. There is also an area of concern with the possibility that an oil layer on the ice surface would change the albedo, even to complete melting of the ice pack. This would have drastic worldwide climatological effects (Campbell and Martin, 1973). Countertheories have been proposed arguing that other forces, "closing of oil-covered leads", would tend to minimize spill dispersal and albedo changes (Clark and MacLeod, 1977). This topic remains open to controversy. Regardless, probability seems high that oil will be entrained underneath and within ice pockets, degradation will be greatly slowed, and the oil will persist for long time periods. As the ice breaks up, oil will migrate to the surface, increasing the melt rate, and be dispersed laterally by oil-water flow.

Droplet formation

The formation of oil droplets which become dispersed within the water column after an oil spill is not understood sufficiently to make quantitative predictions about the number or size distribution of droplets. Some experiments have been performed in laboratory systems, and some measurements have been taken after oil spills. Forrester (1971) reports the distribution of suspended oil droplets in 10 μm increments between 10-85 μm after the spill of the tanker *Arrow*. Theoretically, drops form when a liquid is spread into a film or filament which is unstable due to interfacial tension caused by the decrease in surface of the final system from the initial (Stokes and Harvey, 1973). When a drop is exposed to a sustained moderate shear, it may maintain a fairly large surface area for a time, but when the shear is reduced, the interfacial tension will induce the formation of smaller, spherical droplets. High shear will also cause droplets to break up. Thus, intermittent shear together with short calm periods will promote emulsification (Taylor, 1934). At sea, the main cause of droplet formation during an oil spill is wave-generated turbulence. The greater the wave energy, presumably the greater the droplet formation, but the precise correlation has not been established yet.

APPENDIX III

FECAL PELLETS AS TRANSFER MECHANISMS

Introduction

In marine systems, water layers are stratified much of the year along density gradients caused by differences in salinity and temperature. As phytoplankton in the photic zone bloom, the nutrient content of the surface waters becomes exhausted. When the phytoplankton become senescent and die, or are cropped by zooplankton, nutrients are removed from the photic zone. The sediments become a nutrient sink, and the primary production in the system is nutrient limited until the stratification in the water column is overturned. In these systems, zooplankton play an important role in providing some turnover of nutrients. As they graze upon phytoplankton at the surface, their excretory products rejuvenate the nutrients the phytoplankton are depleting.

The fecal pellets of zooplankton contain a good percentage of organic material. As they sink, they become colonized by bacteria, adding to the nutritive value of the pellet. These fecal pellets are an important food source for other animals in the water column and for benthic fauna (Johannes and Satomi, 1966). In a study of the nutritive value of fecal pellets of a crustacean shrimp (*Palaemonetes pugio*), feces were found to weigh 35% of the ingested food mass. Twenty percent of the fecal material was organic carbon with protein predominating. Lipid comprised 2.5% of the dry weight of feces. When the feces were held in the dark, autolysis, solution, and bacterial respiration resulted in a decrease in percentage of all organic constituents. The rate of production of

organic matter in the feces probably exceeds the rate of production of organic matter in herbivore tissue (Johannes and Satomi, 1966).

Fecal Transport

There are several things which illustrate the effectiveness of fecal pellets as a transfer mechanism. One of these is the presence of viable, surface photosynthetic forms deep within the aphotic zone. The sinking rate of the phytoplankter alone would be too slow for the cell still to be viable at that depth. The second phenomena is instances of annual sediment varving only explicable by an accelerated sinking rate of the phytoplankton debris composing the sediment. Another example is the deposition of certain phytoplankters contributing to sedimentary ooze formation. A contemporary phenomena is the presence of recently radioactive particles in deep oceanic layers (Higgo *et al.*, 1977). There are several mechanisms which might contribute to an acceleration of sinking rates: density inversion currents, aggregations of cells, downwelling, and descent of fecal pellets. Fecal pellets appear to be the most ubiquitous and well-demonstrated mechanism (Smayda, 1971).

Fecal pellets collected in the deep waters of the eastern tropical Pacific contained mainly siliceous plankton remains but also some coccoliths (calcareous) showing good to moderate preservation. Some coccolith-bearing fecal matter reached the seafloor well below the carbonate compensation depth. Thus, geochemically, fecal pellet transfer may be the major mechanism by which typical concentration profiles for nutrients (nutrients which would otherwise not be present, or present in a

different form) are established in the deep ocean. The resultant profiles show low concentrations of nitrate, phosphate, and silicate, as well as decreased values of alkalinity in the uppermost waters (Rolh *et al.*, 1975).

Fecal pellets are also an important transport mechanism in freshwater systems, illustrated by a study conducted on Lake Michigan. The significance of feces was shown by their rapid settling velocity (4.7 m day^{-1}) and their turnover rate (700-3,000 times $month^{-1}$). This turnover rate is 2-3 orders of magnitude faster than that of the freshwater phytoplankton in the euphotic zone (2-3 times $month^{-1}$) (Ferrante and Parker, 1977).

Fecal Production Rate Predictions

Fecal pellets serve the purpose of removing the portion of ingested material not assimilated from the digestive system and from the body. Therefore, the production of fecal pellets depends on the quality and quantity of ingested material and the assimilation efficiency of the animal. Conover (1966) reports that he found no relation between the amount of food offered or ingested, or an increase in temperature; and the percent assimilated. Other authors (Steele, 1974; Turner, 1977a) have suggested that as ingestion increases, assimilation decreases. Assimilation efficiencies range from 0.5 to 0.7 assimilated of the total ingested (Steele, 1974). The number of pellets and the size of pellets are the result of these metabolic variables but need not be included in mass flux calculations. Appendix Table III.1 gives observations of fecal pellets reported in the literature.

APPENDIX TABLE III.1. Feces.

Zooplankter species	Fecal Pellet Dimensions	Fecal Production Rate	Pellets per area	Source
Meganyctiphanes norvegica		1.8 to 5.1% dry body wt day^{-1}	650 pellets m^{-2} per day	Elder & Fowler, 1977
Fresh water copepods	80 to 160 µm long, 150 µm in diameter			Ferrante & Parker, 1977
Calanoid sp.	1.5 x 0.15 mm			Gauld, 1957
Acartia tonsa and *clausi*	200 x 40 µm	91 day^{-1}		Honjo & Roman, 1978
Calanus finmarchicus	950 µm in length	12 $hour^{-1}$ maximum		Marshall & Orr, 1955
Pontella meadii	274-862 µm in length, 59 to 239 µm wide	1.2 pellets $hour^{-1}$		Turner, 1977a,b
205 µm sediment trap in Bahamas	241 µm in length, 109 µm in diameter		650 pellets m^{-2} per day	Wiebe *et al.*, 1976
Temora turbinata		80 to 120^{-1} day	1.2 to 3.2 x 10^5 pellets m^{-2} day^{-1} in productive area; 1000 pellets m^{-2} day^{-1} open ocean	Paffenhofer & Knowles, 1979

APPENDIX IV

TRANSFER TO THE SEDIMENTS

In the marine system, flux to the sediments is transformed (biologically) mainly at or just beneath the sediment surface. Beneath this level the sediment becomes oxygen-limited and other molecules are utilized as electron acceptors, with sulfate being the last utilized. At this point of sulfate usage the system is anoxic. The rate of sulfate reduction in sediments is generally found to be directly proportional to the rate of sedimentation. However, the supply of dissolved sulfate in most sediments runs out before all potentially available organic compounds can be utilized (Berner, 1978). The rates of sulfate reduction range from extensive removal in the period of a month in nearshore areas where organic sedimentation is rapid, to periods of several million years in pelagic regions (Goldhaber and Kaplan, 1975). Since organics are not limiting, this suggests hydrocarbons in feces would not perturb degradation processes but would be trapped in the sediment layers.

In deep waters oxygen consumption is less, and more of the consumption is due to chemical processes rather than animal. Smith and Teal (1973) in an examination of water at 1850 m found that oxygen uptake was 2 orders of magnitude less than that found in shallow shelf areas. Deep sediments thus might be more perturbed by a sudden increase in organic loading than shallow waters. Lower oxygen levels might force a shift to an anoxic regime.

Hargrave (1978) in a study of sediment decomposition, found that the oxidation of the settled organic matter was largely complete within the

year of deposition. However, except during the summer, the organic matter was resistant to rapid aerobic decomposition. The decomposition proceeded to a final stage where often greater than 50% of the organic matter remained with little further decomposition. A 1-2 month delay generally existed between deposition of particulate matter and the maximum rate of oxygen consumption by the sediments. Respiration, except in May, was 1-2 mg O_2 g^{-1} org^{-1} hr^{-1}. Again, this demonstrates sediment hydrocarbon trapping and the potential for forcing the system to go anoxic.

The organic matter naturally falling to the benthos in Resurrection Bay, Alaska, was estimated by Heggie (1973) as 234-658 mg C m^{-2} day^{-1}. Turner (1977b) estimates carbon loading on the sediments in the Gulf of Mexico as 0.03 to 0.20 mg C m^{-2} day^{-1}.

The nutrient flux caused by fecal pellets has been measured for other nutrients and pollutants. Elder and Fowler (1977) measured the rate of fecal released PCB's (polychlorinated biphenyls) from $5.2 \cdot 10^{-5}$ to $15 \cdot 10^{-5}$ µg m^{-3} day^{-1}. They calculate the PCB sedimentation rate as 1.4-4.1 µg m^{-2} yr^{-1}.

Increases in carbon loading on the sediments have been found to cause changes in the anoxic layer. Seki *et al.* (1974) report the formation of an anoxic zone in Tokyo Bay following a phytoplankton bloom. However, the major portion of the sedimenting detritus was not composed of fecal pellets but of phytoplankton fragments caused by mechanical destruction during grazing. The production of fecal pellets was one-tenth to one-half that of the phytodetritus. Production of organic

debris was unimportant when the phytoplankton densities were lower than 1.5 g C m^{-3}.

Davies (1975) reports on a Scottish loch in which an ungrazed bloom of Chaetoceros settled in May and caused the top 2 cm to go anoxic. He reports the organic input to the bottom as 28 g C m^{-2} yr^{-1} and total oxygen consumption for the sample area as 132 g O_2 m^{-2} yr^{-1}. Little sediment decomposition appeared in the winter, as benthic animal respiration accounted for the whole of the winter respiration (and only 25% in the summer and spring). These reported cases of anoxic forcing due to increased carbon loading involve greater carbon masses than those dealt with in this model.

APPENDIX V

LABORATORY ANALYSIS OF PLANKTON SAMPLES

Sample Collection

Samples were collected by plankton net tows. Bering Sea samples were obtained in May of 1977, generally by a vertical tow to bottom with a bongo net (mesh 330 µm). The plankton were decanted into a shallow tray and sorted by species. Individual organisms were removed with tweezers and placed in vials which had previously been baked at 500°C to remove all organics. The vials were then frozen until laboratory analysis. Cook Inlet samples were collected in May, 1978 from two stations: one in a biologically productive area and one in an area of low productivity. Stations were occupied for 48 hours, horizontal tows of three-hour duration were made at the low productivity station and vertical tows at the other at 12-hour intervals with a 230 µm net. Another time series was collected with vertical tows at a new station in August, 1978. Tows were decanted into baked jars and frozen. Appendix Table V.1a describes the date and location from which samples were taken.

Sample Analysis

Depending on sample size, the entire frozen sample or a 2-4 ml aliquot of tissue with the associated liquids was placed in 10 ml glass centrifuge tubes with Teflon lined caps. Bering Sea sample size did not always permit dry weight determinations, but for Cook Inlet samples the dry weights were measured. All tools and glassware were rinsed with acetone and three times with hexane before use. Three mls of 10N KOH

APPENDIX TABLE V.1a. Sample description.

Sample #	Sample Description	Location		Date
1	*Parathemisto pacifica*	54°42'	165°59'	5-22-77
2	*Parathemisto pacifica*	59°09.6'	168°38.4'	6-7-77
3	Copepods 1 to 3 mm	57°07'	170°58'	5-23-77
4	Copepods 5 mm	55°33'	58°9'	5-22-77
5	*Calanus glacialis*	54°58'	168°9'	5-22-77
6	Copepod sp.	59°09.6'	168°38.4'	6-7-77
7	Copepod sp.	59°57.2'	168°55.7'	6-7-77
8	Copepod sp.	56°30'	167°41'	6-8-77
	Cook Inlet Mixed Plankton Time Series			
9	0 hr.	60°28.2'	152°12.2'	5-12-78
10	12 hr.			
11	24 hr.			
12	36 hr.			
13	48 hr.			
14	0 hr.	59°39.4'	151°45.9'	5-7-78
15	12 hr.			
16	24 hr.			
17	36 hr.			
18	48 hr.			
19	0 hr. duplicate	59°39.4'	151°45.9'	5-7-78
20	12 hr. duplicate			

and three mls of hexane were then added to the tubes, and they were placed in a water bath for 3 hours at 90°C. Tubes were shaken at regular intervals. After 3 hours the samples were placed in an ice bath to cool. When cool, the hexane phase was drawn off with a rinsed glass syringe and stored in rinsed glass pear flasks. Three mls of hexane were added, tubes were shaken, and then centrifuged at 2300 rpm for 10 minutes. The hexane phase was again decanted, and this procedure repeated twice again. If emulsions were a problem, samples were reheated and recooled. Once extraction was complete, samples were stored overnight in the dark and dried over a small amount of Na_2SO_4. Samples were later concentrated to 0.5 ml and placed on silica gel columns. The columns were constructed by packing 5 grams of 5% water de-activated silica gel in a hexane slurry into 25 ml burets (140 mm x 10.5 mm). Samples were eluted in two fractions. The first solvent used was hexane, the second 20% methylene chloride in hexane. Elutant volumes were specific for each batch of silica gel and were tested prior to use in order to prevent tailing of the alkane fraction into the aromatics. The hexane fraction was usually 10 ml; the second fraction generally 14 ml. Each fraction was concentrated to approximately 1 ml and 1 µℓ injected into a Hewlett-Packard 5710 gas chromatograph (GC) with 40 m support coated open tubular (SCOT) column with inner diameter 0.64 mm. The columns are coated with a slurry of: 1% weight/volume OV-101, 0.1% w/v carbowax 20M, and 2% w/v silonox 101 in chloroform. Helium carrier gas flow rate is maintained at 30 ml min^{-1}, injector and detector temperatures at 300°C. The column temperature was programmed from 70 to 270°C at 8° per minute.

Computations of hydrocarbon concentrations and compound identification were made by calibration against a standard alkane and aromatic mixture injected into the GC before each day's run. The standard contains the following compounds: naphthalene, phenanthrene, octadecane, fluoranthene, docosane, octacosane, perylene, and dotriacontane. The total weight of hydrocarbons was 0.9177 mg per ml of hexane. Quantification was made through the use of a digital integrator (Hewlett-Packard Model 3380 or 3385). Hydrocarbon identifications were also verified by use of mass spectrometer (Hewlett-Packard 5930).

Duplicate analyses were performed on some of the Cook Inlet samples and the aliquot size was also varied to see if there was a variability caused by small sample size. Efficiency of extraction was examined by spiking samples with a known hydrocarbon concentration and evaluating the recovery. Blanks (tubes with solvents, no biota) were run with each batch of samples, also accompanied by a spiked blank.

Results and Discussion of Baseline Hydrocarbon Analysis

Results of these hydrocarbon analyses of Alaskan zooplankton appear to correspond fairly well with the literature discussion of biogenic hydrocarbons in the second Appendix to this thesis. Data is listed in Appendix Table V.1b. The percentage dry weight of wet weight is generally given as close to 20% (Omori, 1969) so these samples are somewhat low in this respect. This may be due to the small amount of tissue actually sampled. Water carried throughout the handling process and frozen with the sample becomes important when total tissue weight is small, thus

APPENDIX TABLE V.1b. Results of plankton analysis.

Sample No.	Wet wt grams	Dry wt grams	% dry wt of wet	Biota peak ID & weight mg	Run biota recovery alkanes	Blank recovery alkanes	Pristane PPM
1	0.16100	0.012*		pristane 0.02109	82%	64%	1800
2	0.52545	0.040*		pristane 0.00304			76
3	0.38054	0.04019	10.5	pristane 0.26632	62%	75%	6600
4	0.69384	0.04397	6.3	pristane 0.01358			309
5	1.08600	0.08059	8.3	pristane 0.35558			4400
6	2.41659	0.21150	8.8	pristane 0.27762	32%	54%	1300
7	1.34851	0.24973	18.5	pristane 0.11313			450
8	1.69725	0.18130	10.7	pristane 0.47265			2600
9	1.63723	0.11624	7.0	pristane 0.00354	54%	76%	31
10	1.49052	0.14100	9.5	pristane 0.00320			23
11	1.43841	0.15796	8.6	pristane 0.00023			1.5
12	1.29342	0.12381	7.6	pristane 0.00280			23
13	1.40953	0.16274	9.7	pristane 0.00068			4.2
14	3.98447	0.17878	4.5	pristane 0.00497	39%	32%	29
15	3.91070	0.17121	4.4	none			
16	3.78546	0.16645	4.4	none			
17	3.91831	0.19681	4.9	pristane 0.00358			18
18	3.87880	0.20371	5.1	pristane 0.00018			1.0
19	4.03105	0.18087	4.5	pristane 0.00905	61%	51%	50
20	3.76843	0.16581	4.4	none			

*Using 7.7% conversion factor averaged from other data.

increasing the wet weight erroneously. Pristane was the only aliphatic compound found, agreeing with Gastaud's (1977) observation that pristane was the major compound of the hydrocarbon fraction of Arctic zooplankton. Taking lipid content to be 20% of the dry weight, the pristane concentration for all copepod samples ranged from 0.1 to 3% of the lipids. The assumption that the lipid fraction is 20% of the dry weight is probably low for Arctic copepods. Lee and Hirota (1973) found values ranging from 30 to 70% of the dry weight. Pristane has been reported to occur in concentrations of 1-3% of the body fat (Blumer *et al.*, 1963). The same procedure when applied to the Cook Inlet samples produces pristane concentrations of 0.01% or less. These samples, however, are mixed plankton samples (also containing phytoplankton) and pristane would not be expected to appear in the high concentrations it manifests in zooplankton.

Unfortunately, the limited number of samples available, and their small size, cast the replicability and accuracy of this data in doubt. Replicate analyses, and the analyses performed on larger aliquots of the Cook Inlet samples were similar to the original analyses but not enough replicates were performed for statistical applications. The use of a three hour horizontal tow is suspect as a representative sampling device. It is possible that avoidance behavior could occur. The tows made in the low productivity zone collected very little biomass. For samples predominantly phytoplankton, the chance variations in zooplankters caught could significantly alter the pristane content. Variations do not appear to correlate with time of day.

The samples were not always sorted and organisms identified prior to freezing; thus it is difficult to apply this data to trophic levels or food web transfer, except again to say that pristane is the prominent hydrocarbon product.

Recoveries of spiked blanks were similar to spiked biota, showing that biogenic compounds are not hindering the extraction of hydrocarbons.

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